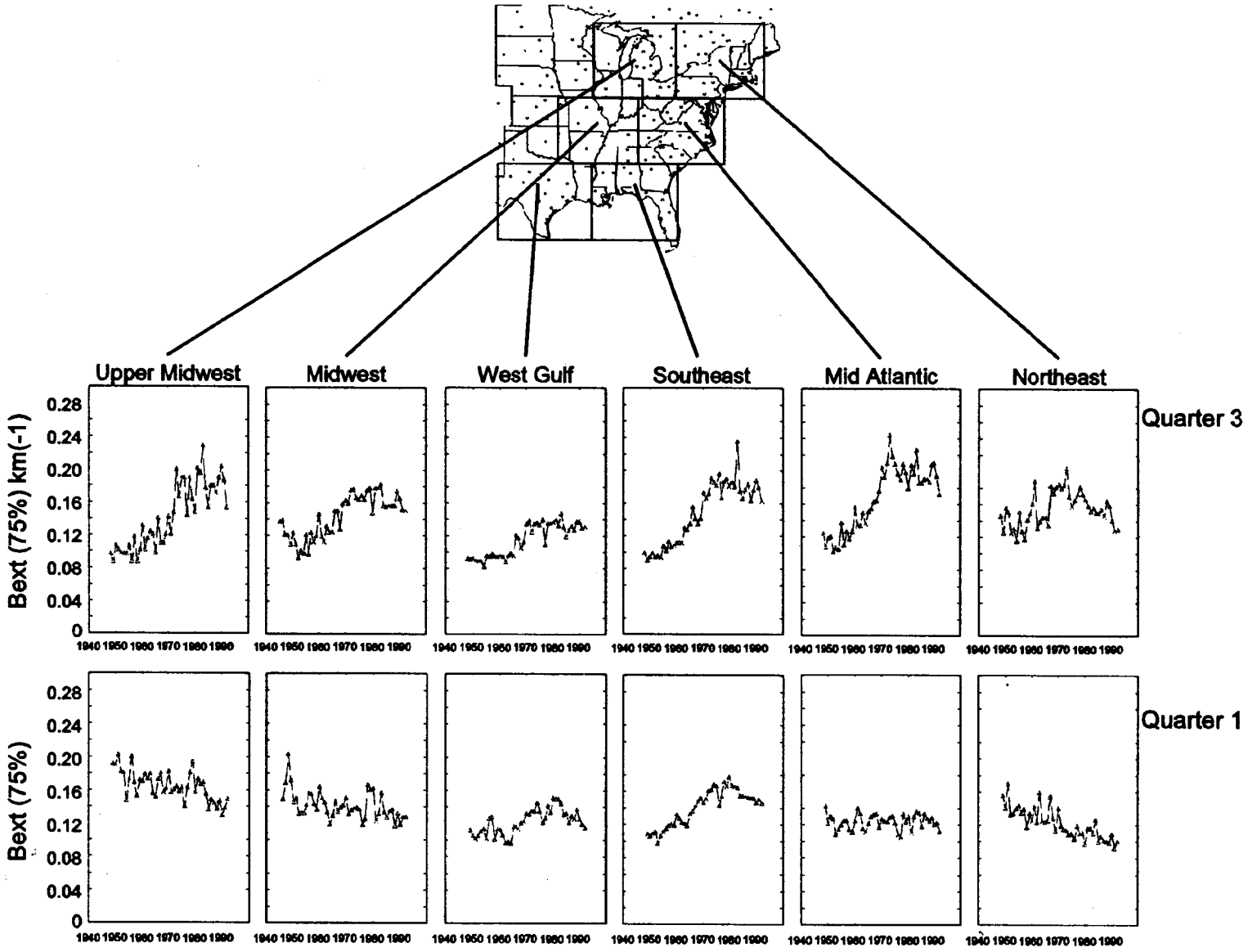

Figure 6-113. Secular haze trends (1960 to 1992) for six eastern U.S. regions, summer (Q1) and winter (Q3)

Mountains National Park, provide useful information on the regional background of sulfate (Eldred and Cahill, 1994; Cahill et al., 1996b). As shown in Figure 6-114, there is a distinct increase in sulfate. This increase can be correlated with increases in SO_2 emissions in the summer from power plants in the Tennessee Valley (Cahill et al., 1996b). The increased emissions may be related to an increase in demand for power for air conditioning. The increase in regional background will impact urban centers along the eastern U.S. Visibility measurements over the northeastern U.S. show an increase in haze from 1960 to 1970 in both winter and summer. Between 1970 and 1983, there was a decrease in haze in the winter but little change during the summer (Husar and Wilson, 1993; Husar et al., 1994). Concern has been expressed that the indicated trends may have been impacted, or even produced, by changes in monitoring protocols (White, 1996a,b). However, these issues have been addressed by Cahill et al. (1996b).

6.10.2.3 Philadelphia

Philadelphia is of special interest because of the extensive monitoring conducted there and the use of Philadelphia data in epidemiological studies. Extensive measurements of TSP have been conducted in Philadelphia. Several data sets have been combined to give an indication of long-term trends in Philadelphia (Figure 6-115). The TSP data set was construed from the AIRS data base (Wyzga and Lipfert , 1996; Li and Roth, 1995). There was a steady decrease in TSP from 1973 to 1983 with variable but slightly increasing TSP levels between 1983 and 1990.

Fine PM was estimated from the Inhalable Particle Network (Rodes and Evans, 1985) from 1980 to 1983, from AIRS (AIRS, 1995), from 1987 to 1990, and from the Harvard Data Base (Koutrakis, 1996) for 1993 and 1994. During the period 3/79 to 12/83, the Inhalable Particulate Network conducted measurements in Philadelphia with dichotomous samplers. These used 15 μm upper cut points except for a period at the end of the study (3/82 to 12/83) when two co-located PM_{10} samplers were run at one site. The IPN data set allows construction of four annual averages for 1980 through 1983 by averaging $PM_{2.5}$ data from $PM_{15}/PM_{2.5}$ dichotomous samplers from the several IPN sites across Philadelphia. These are shown in Figure 6-115, along with the one year of $PM_{2.5}$ data from $PM_{10}/PM_{2.5}$ dichotomous samplers at the South Broad St. site.

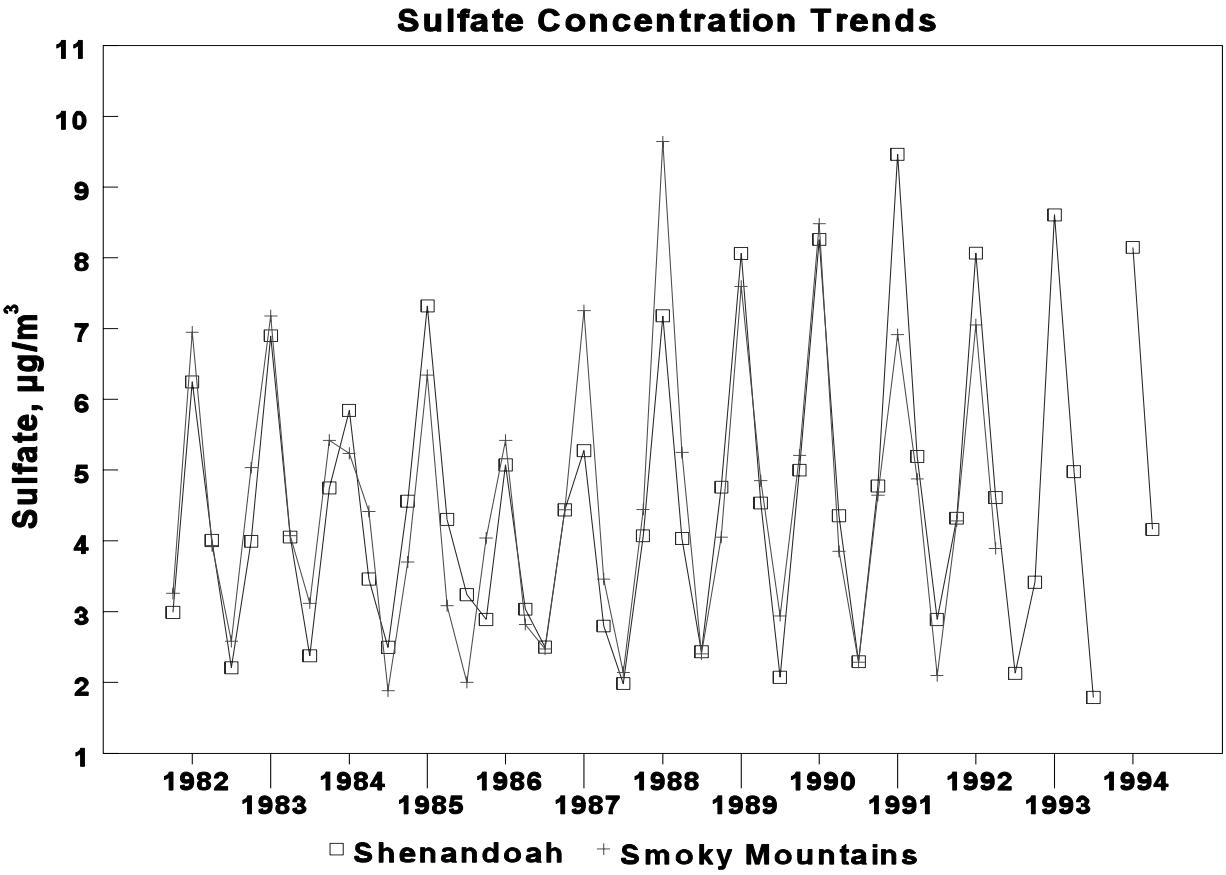

Figure 6-114. Eastern U. S. regional background trend of sulfate indicated by seasonal trend data from Shenadoah and Great Smoky Mountains National Parks.

A $PM_{10}/PM_{2.5}$ dichotomous sampler, run in the Philadelphia area from 1987 through 1990 allows annual averages of $PM_{2.5}$ for those years to be added to Figure 6-115. Harvard University measured PM_{10} and $PM_{2.5}$ at the Presbyterian Home site from 5/92 to 5/92 allowing annual averages for 93 and 94 to be added to the graph. Since $PM_{2.5}$ is expected to be relatively uniform across Philadelphia (Wilson and Suh, 1996), this data can be used to estimate a $PM_{2.5}$ trend from 1979 to 1994. A downward trend is indicated.

The samplers were not at the same sites during the different time periods. Since $PM_{(10-2.5)}$ does not seem to be uniform across Philadelphia (Wilson and Suh, 1996), no PM_{10} or $PM_{(10-2.5)}$ trend could be constructed. Comparisons of PM_{10} and $PM_{(10-2.5)}$ and $PM_{2.5}/PM_{10}$ (Figure 6-116) for 1983 and 1993 are shown. Differences in $PM_{(10-2.5)}$ and the ratio of

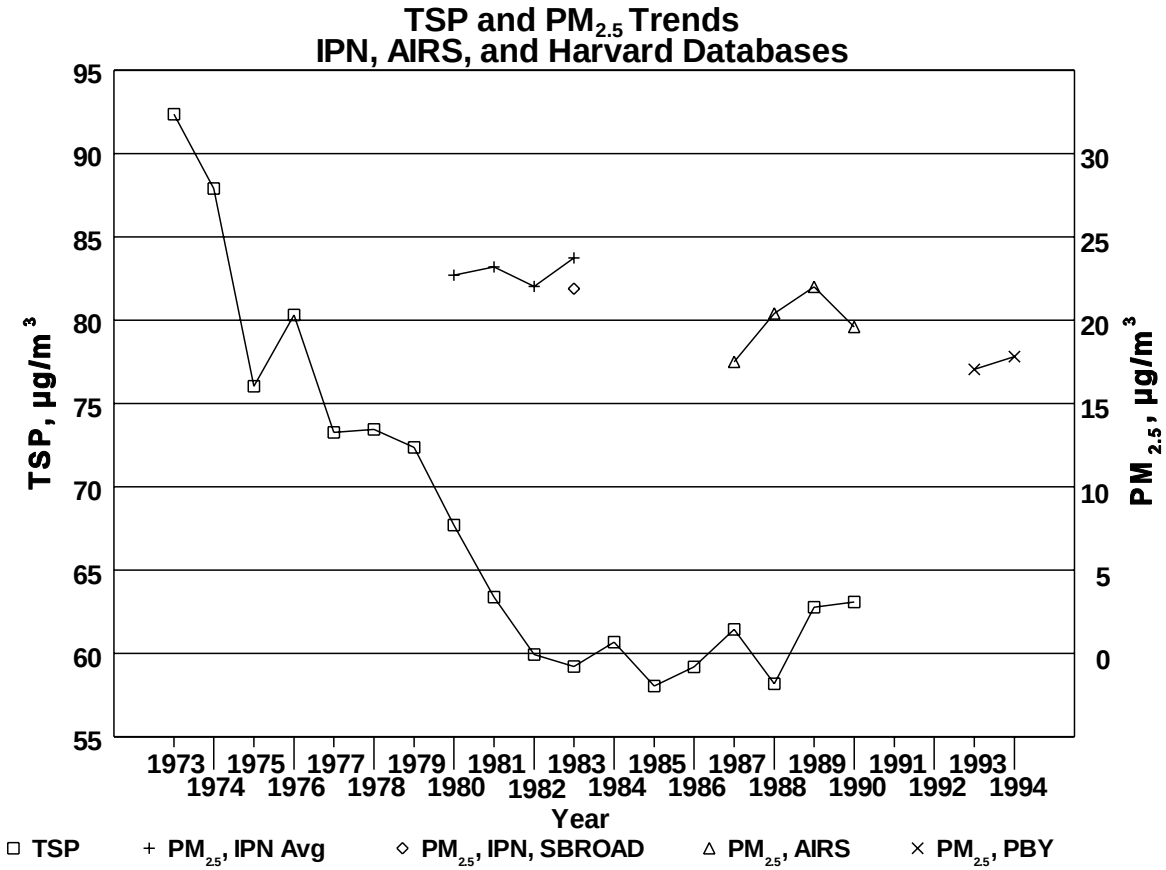

Figure 6-115. TSP and $PM^{2.5}$ trend data for the city of Philadlphia from AIRS, IPN, and Harvard database.

$PM_{2.5}/PM_{10}$ may represent geographical differences in the coarse fraction of PM_{10} as well as relative changes in $PM_{2.5}$ and $PM_{(10-2.5)}$.

6.10.2.4 Harvard Six-Cities Study

During 1979 to 1986, the Harvard School of Public Health measured particulate matter in 6 cities in eastern and central United States (Spengler et al., 1986b; Neas, 1996). Means and 90^{th} percentiles for fine, coarse, PM_{15}, and TSP are shown in Figures 6-117 to 6-119. (Measurements were made with dichotomous samplers with a 15 μm diameter cut point from 1979 to 1984 and with a 10μm diameter cut point from 1984 to 1986. The coarse fractions of PM_{10} and PM_{15} were not significantly different during the overlapping year.) In the dirtier cities, Steubenville, St. Louis, and Harrison, there were decreases in all PM indicators, especially in the earlier years.

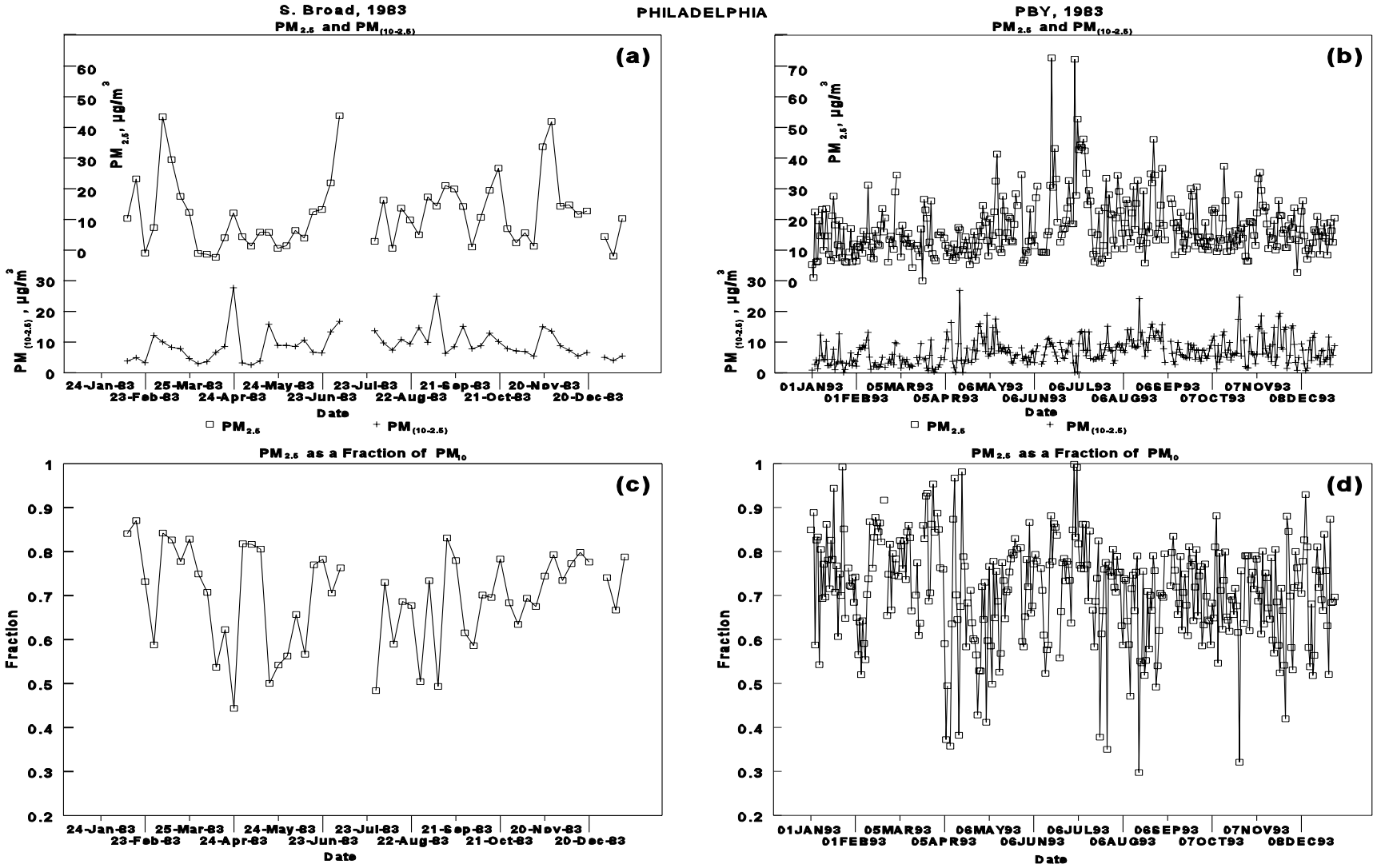

Figure 6-116. Comparison of fine and coarse particle parameters in Philadelphia in 1983 and 1993: (a) $PM_{2.5}$ and $PM_{(10-2.5)}$ at South Broad St. site, 1983; (b) $PM_{2.5}/PM_{10}$ at South Broad St. site, 1983; (c) $PM_{2.5}$ and $PM_{(10-2.5)}$ at Presbyterian Home site, 1993; (d) $PM_{2.5}/PM_{10}$ at Presbyterian Home Site, 1993.

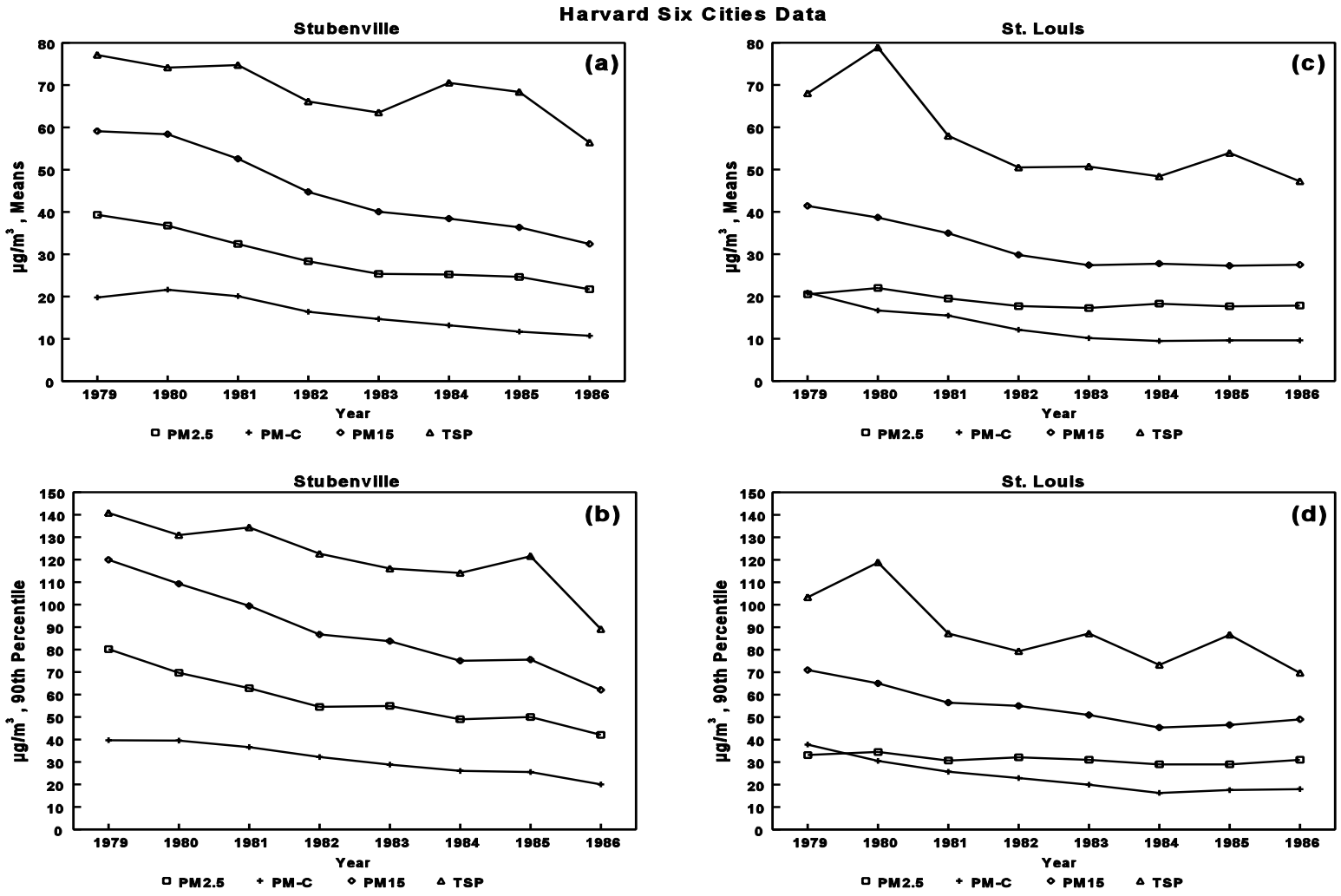

Figure 6-117. Trend data from the Harvard Six-Cities Study: (a) Steubenville, fine, coarse, PM_{15}, and TSP means; (b) Steubenville, fine, coarse, PM_{15}, and TSP 90th percentiles; (c) St. Louis, fine, coarse, PM_{15}, and TSP means; (d) St. Louis, fine, coarse, PM_{10}, and TSP 90th percentiles.

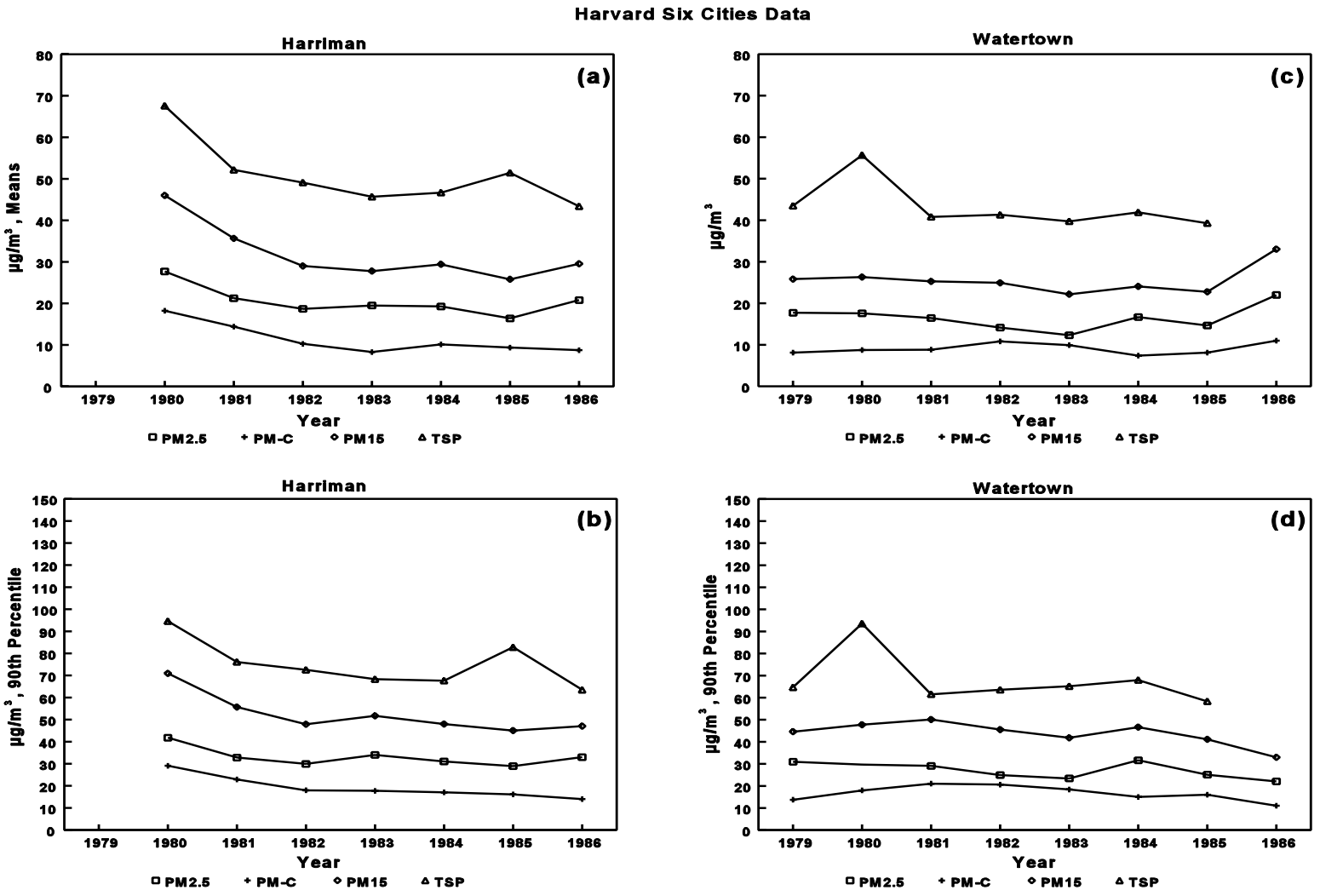

Figure 6-118. Trend data from the Harvard Six-Cities Study: (a) Harriman, fine, coarse, PM_{15}, and TSP means; (b) Harriman, fine, coarse, PM_{15}, and TSP 90th percentiles; (c) Watertown, fine, coarse, PM_{15}, and TSP means; (d) Watertown, fine, coarse, PM_{15}, and TSP 90th percentiles.

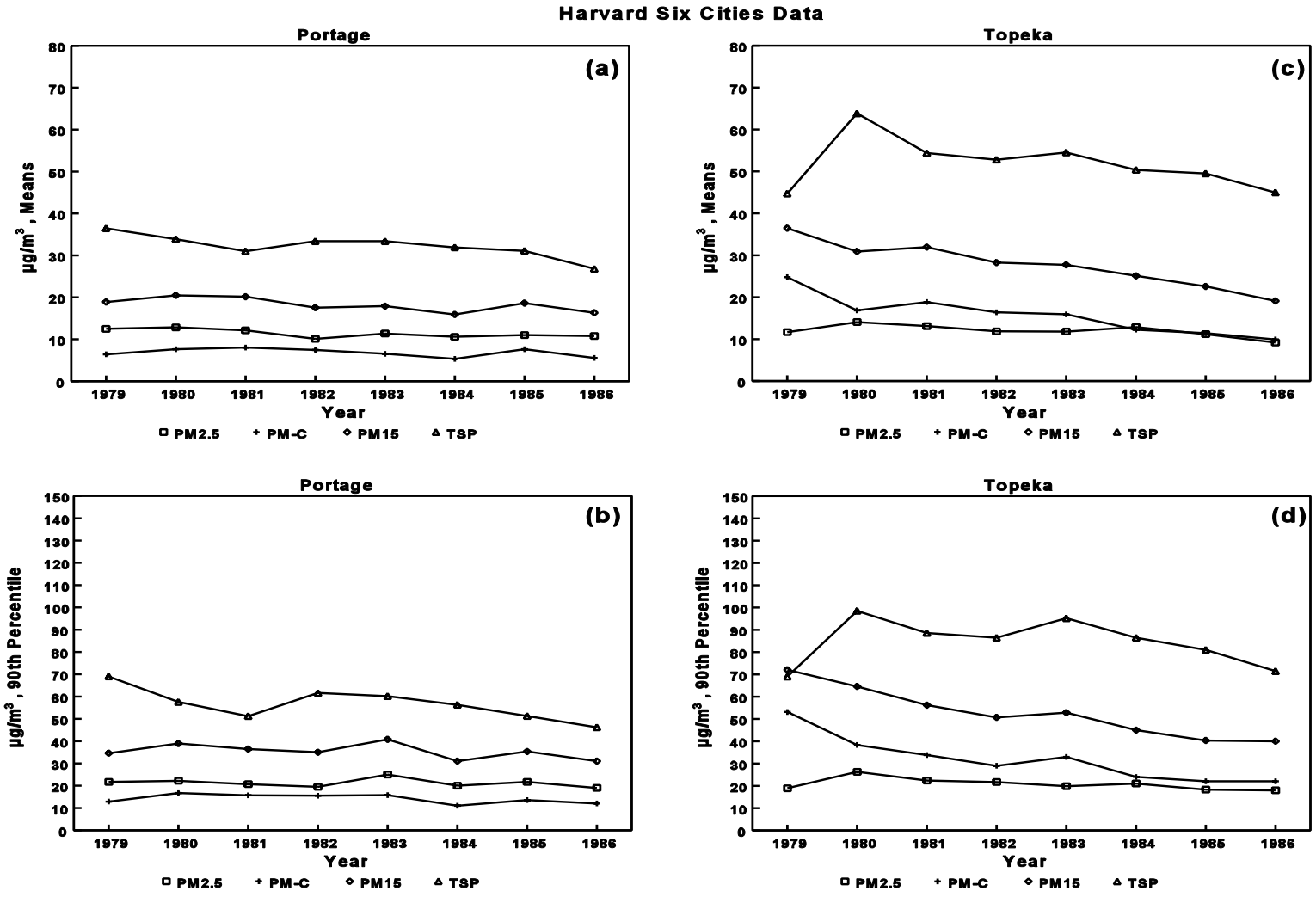

Figure 6-119. Trend data from the Harvard Six-City Study: (a) Portage, fine, coarse, PM_{15}, and TSP means; (b) Portage, fine, coarse, PM_{15}, and total TSP 90th percentiles; (c) Topeka, fine, coarse, PM_{15}, and TSP means; (d) Topeka, fine, coarse, PM_{15}, and TSP 90th percentiles.

There was also an apparent decrease in Topeka, one of the cleaner cities. No trend can be discerned in Watertown or Portage. It is difficult to determine whether there was a greater trend in fine or coarse particles.

6.10.2.5 AIRS

The AIRS data base was searched for sites with 4 or more years of fine and coarse data (AIRS, 1995). Five such sites were found. Values for the mean and the 90th percentile are shown in Figures 6-120 to 6-123. No significant trends are evident in $PM_{2.5}$ or $PM_{(10-2.5)}$ either in the means or the 90th percentile values. PM_{10} and $PM_{(10-2.5)}$ at the dirtier site in New York City do appear to have decreased from 1988 to 1992 but to have increased between 1992 and 1994.

6.10.2.6 California Sites

The California Air Resources Board conducted dichotomous sample measurements, every sixth day, beginning in 1989 at a number of California sites (CARB, 1995). Some results from 8 sites are shown in Figures 6-124 to 6-130. The means (Panel a) and 90th percentile values (Panel b) are given for $PM_{2.5}$, $PM_{(10-2.5)}$, and PM_{10}. Most of the sites show slight downward trends for PM_{10} and both $PM_{2.5}$ and $PM_{(10-2.5)}$.

The California sites are of special interest because of the substantial seasonal and daily variability. The individual every-sixth-day values are plotted for 1991 (plus 1 day in the preceeding and following years)(Panel c). Strong seasonal and daily variation are evident. Based on the every-sixth-day measurements, it would appear that the day-to-day variability at the California sites is higher than in Philadelphia. Also shown is the $PM_{2.5}$ fraction of PM_{10} (Panel d). These ratios are also show a strong seasonal variation.

6.10.3 Interrelations and Correlations

The availability of data on four PM size fractions at several sites for a number of years makes it possible to examine relationships and correlations among $PM_{2.5}$, $PM_{(10-2.5)}$, PM_{10}, and TSP. It is also possible to examine the distribution of values in the upper range and the relationship of the fine fraction to other PM parameters. Sufficient data for these purposes are

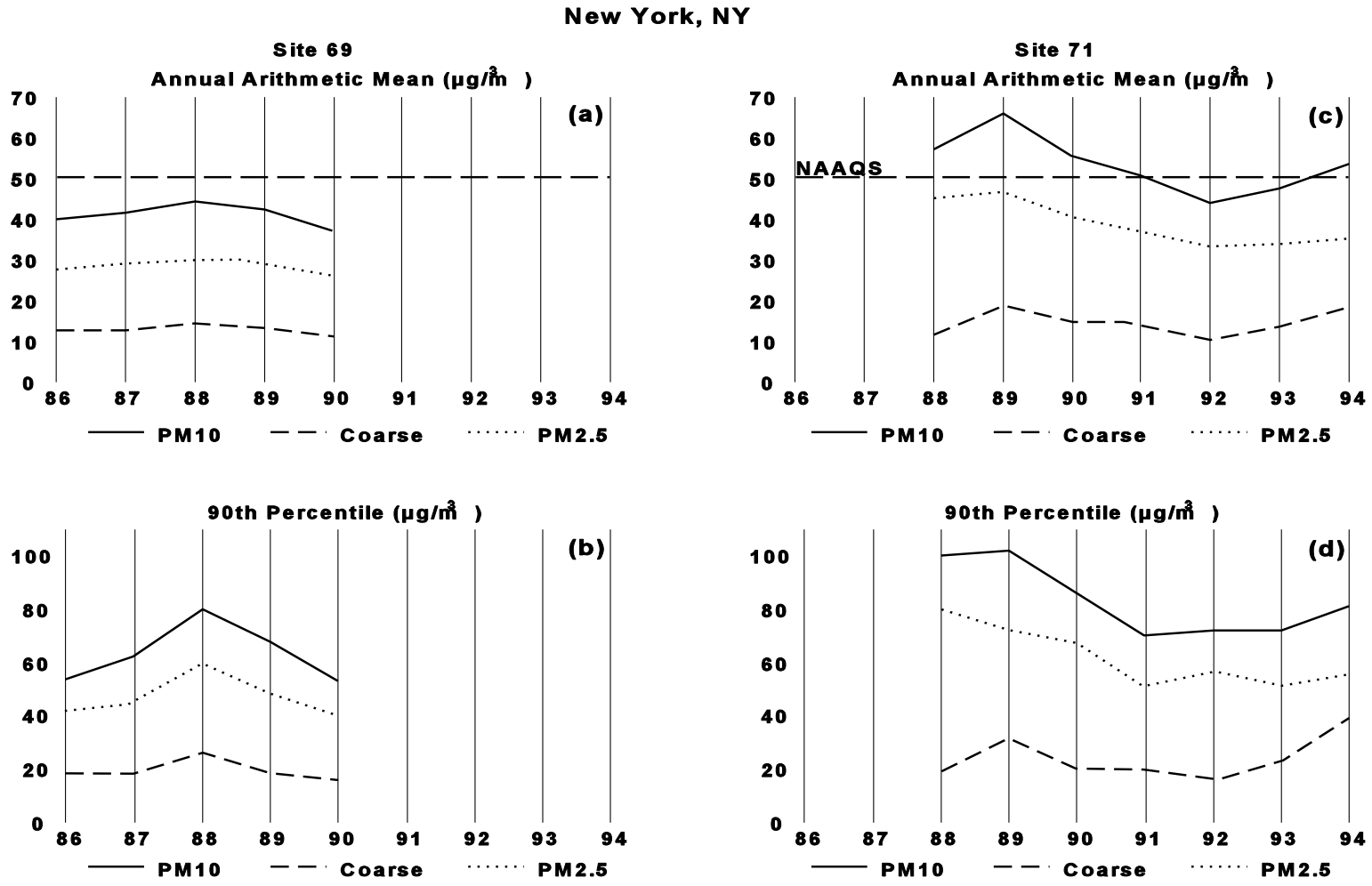

Figure 6-120. Trend data from AIRS: (a) New York City, Site 69, fine, coarse, and PM_{10} means; (b) New York City, Site 69, fine, coarse, and PM_{10} 90th percentiles; (c) New York City, Site 71, fine, coarse, and PM_{10} means; (d) New York City, Site 71, fine, coarse, and PM_{10} 90th percentiles.

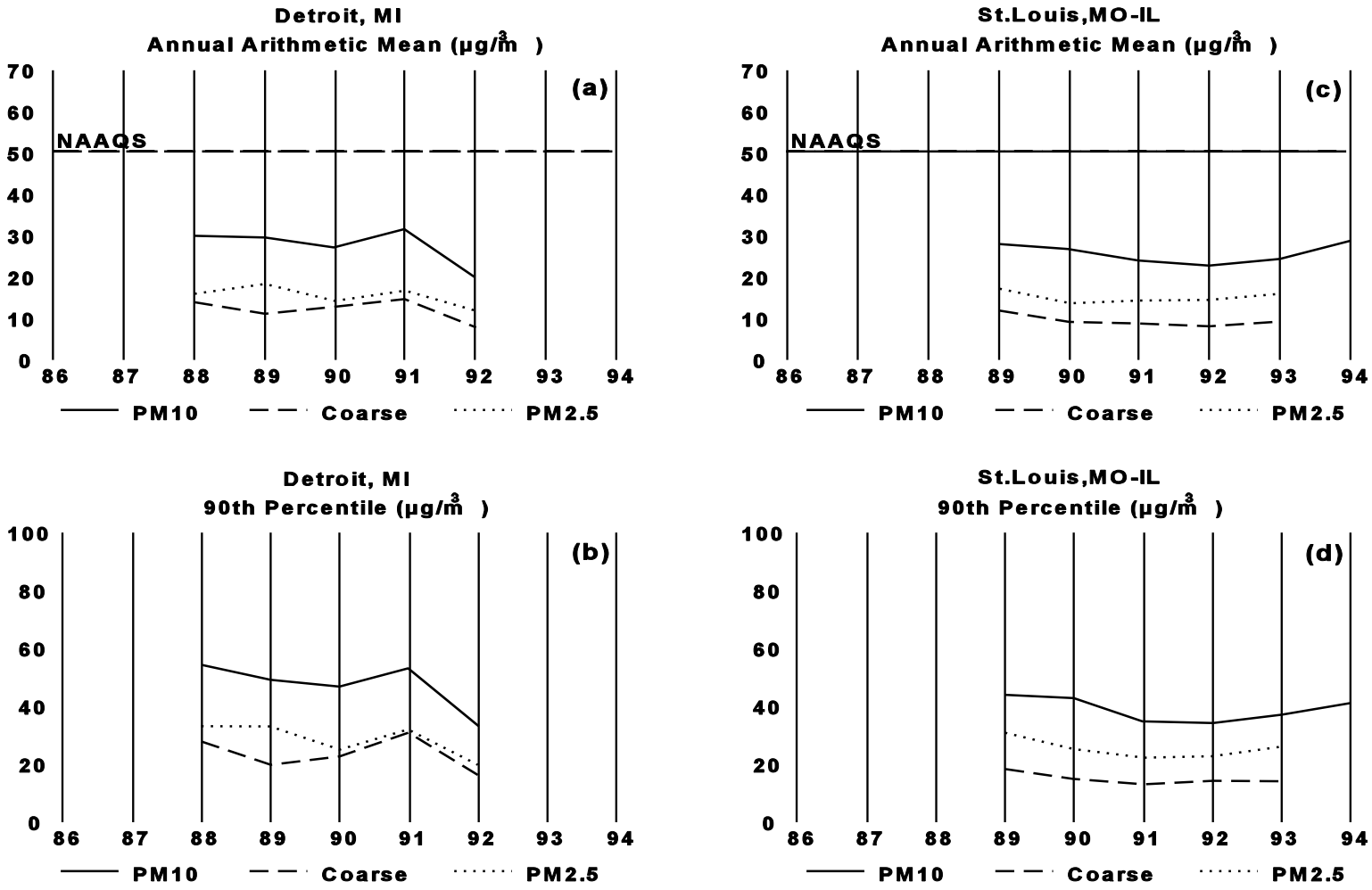

Figure 6-121. Trend data from AIRS: (a) Detroit, fine, coarse, and PM_{10} means; (b) Detroit, fine, coarse, and PM_{10} 90th percentiles; (c) St. Louis, fine, coarse, and PM_{10} means; (d) St. Louis, fine, coarse, and PM_{10} 90th percentiles.

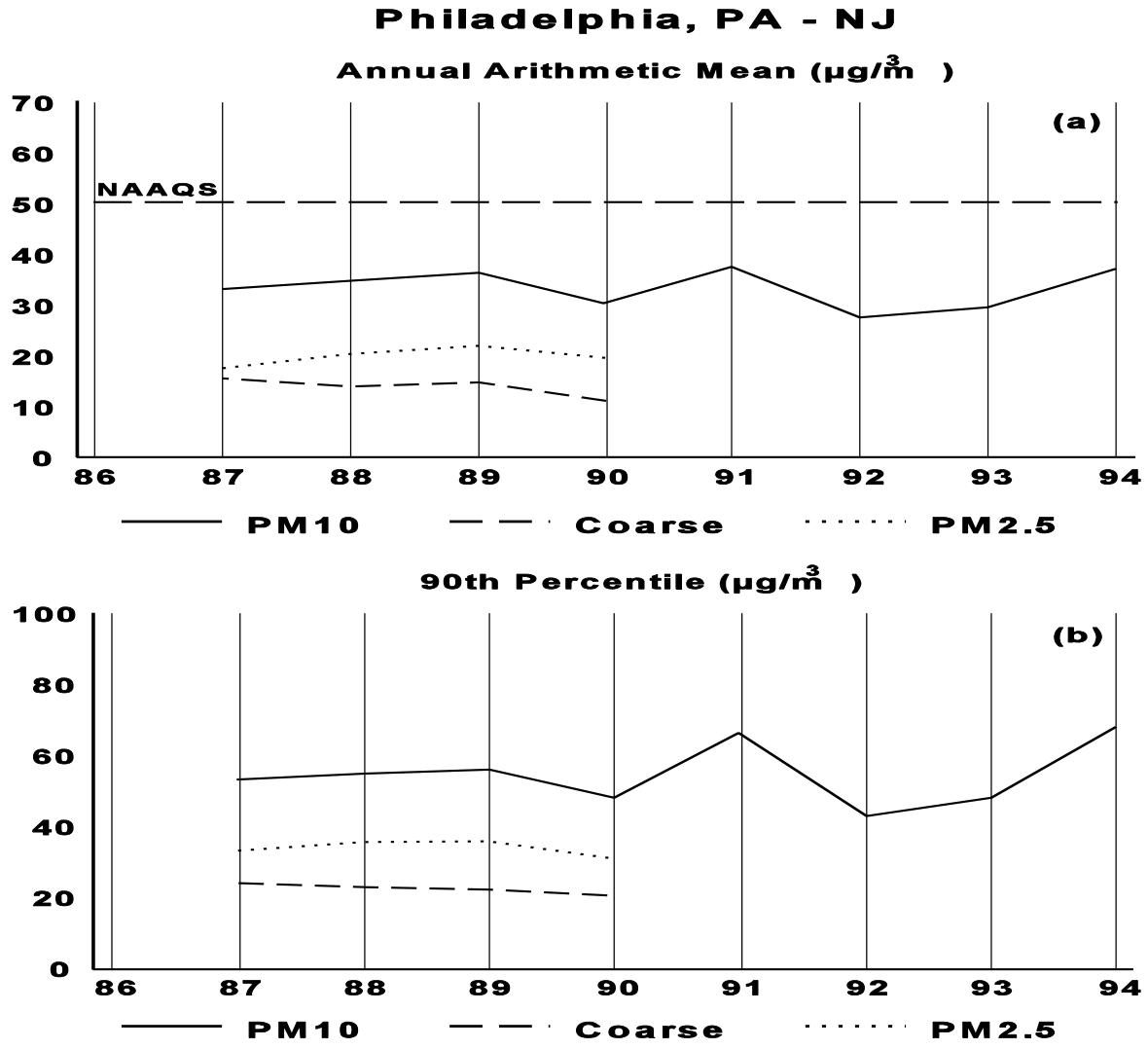

Figure 6-122. Trend data from AIRS: (a) Philadelphia, fine, coarse, and PM_{10} means; (b) Philadelphia, fine, coarse, and PM_{10} 90th percentiles.

available from several sites in California (CARB, 1995) and from Philadelphia (IPN, 1985; AIRS, 1995; Harvard 1995). However, only the Philadelphia data allows examination of the relationship of $PM_{2.5}$ and PM_{10} with TSP.

6.10.3.1 Upper Range of Concentration for Various PM Size Fractions

Some information on the upper range of concentrations and relationships among the four PM size fractions are shown in Tables 6-11 and 6-12. The maximum value; the 2nd, 3rd, 4th,

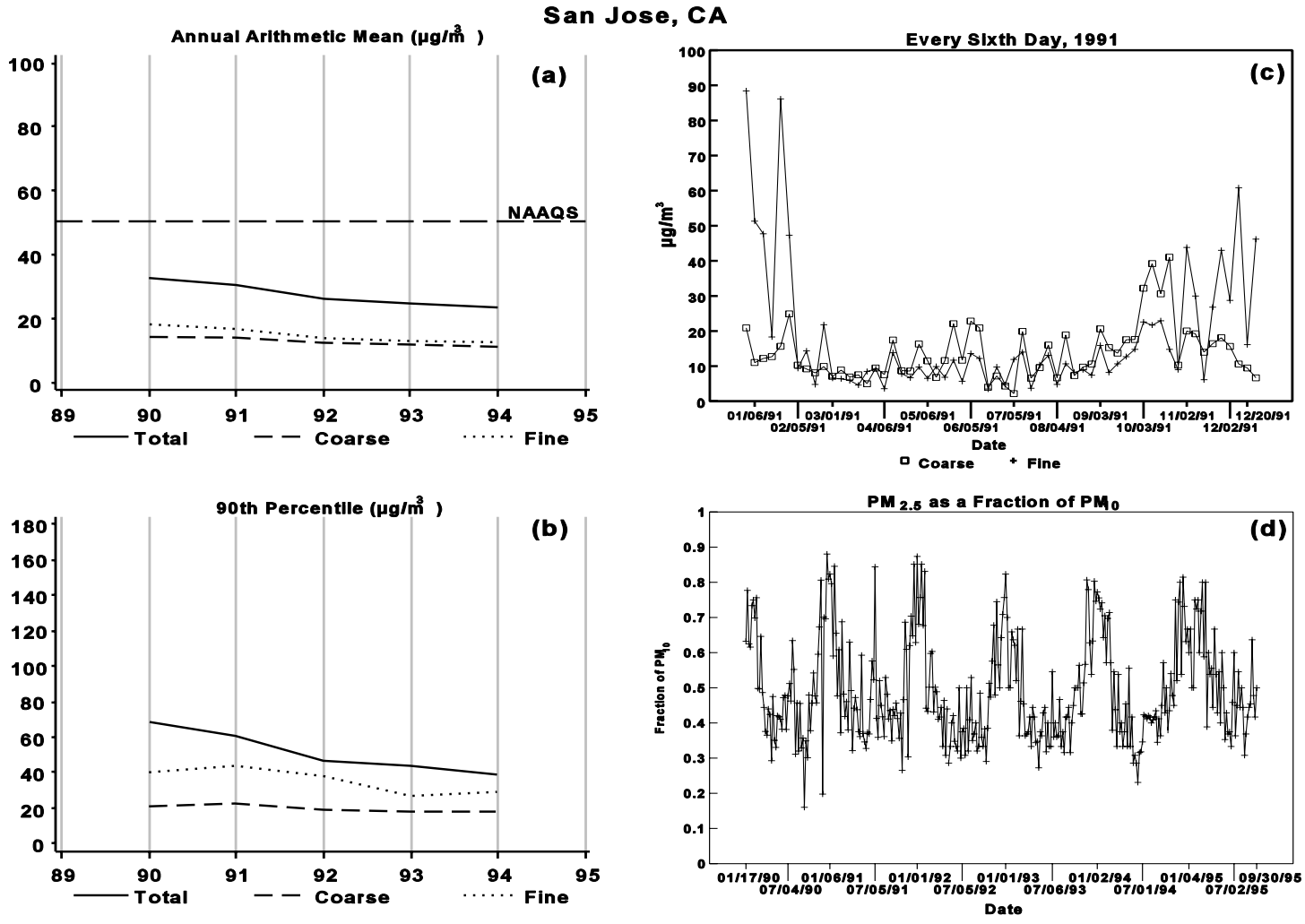

Figure 6-123. Trend data from San Jose from CARB: (a) Fine, coarse and total means; (b) Fine, coarse and total 90th percentiles; (c) Every sixth day fine and coarse mass for 1991; (d) Fine and coarse mass as a fraction of PM_{10}.

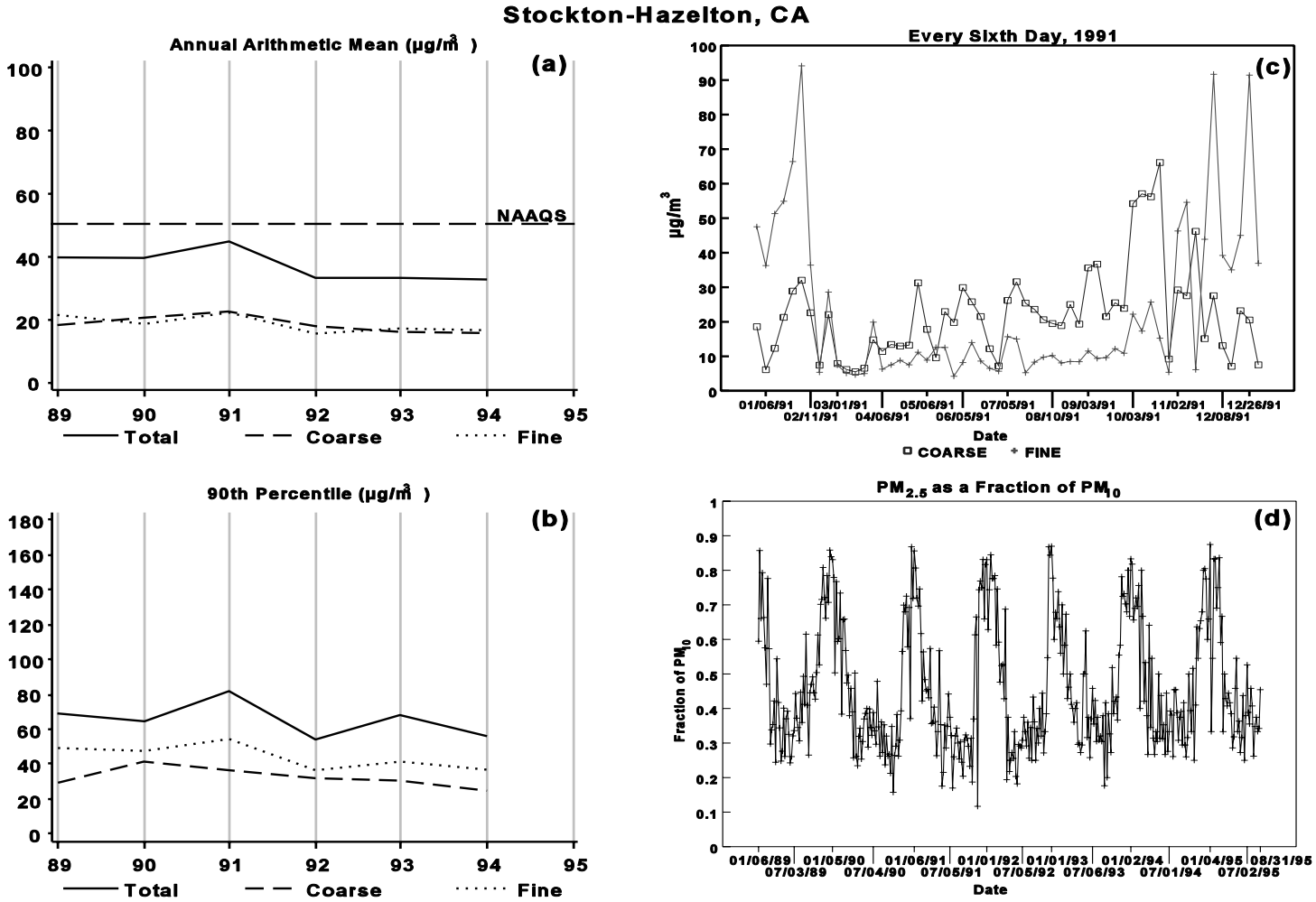

Figure 6-124. Trend data from Stockton-Hazelton from CARB: (a) Fine, coarse and total means; (b) Fine, coarse and total 90th percentiles; (c) Every sixth day fine and coarse mass for 1991; (d) Fine and coarse mass as a fraction of PM_{10}.

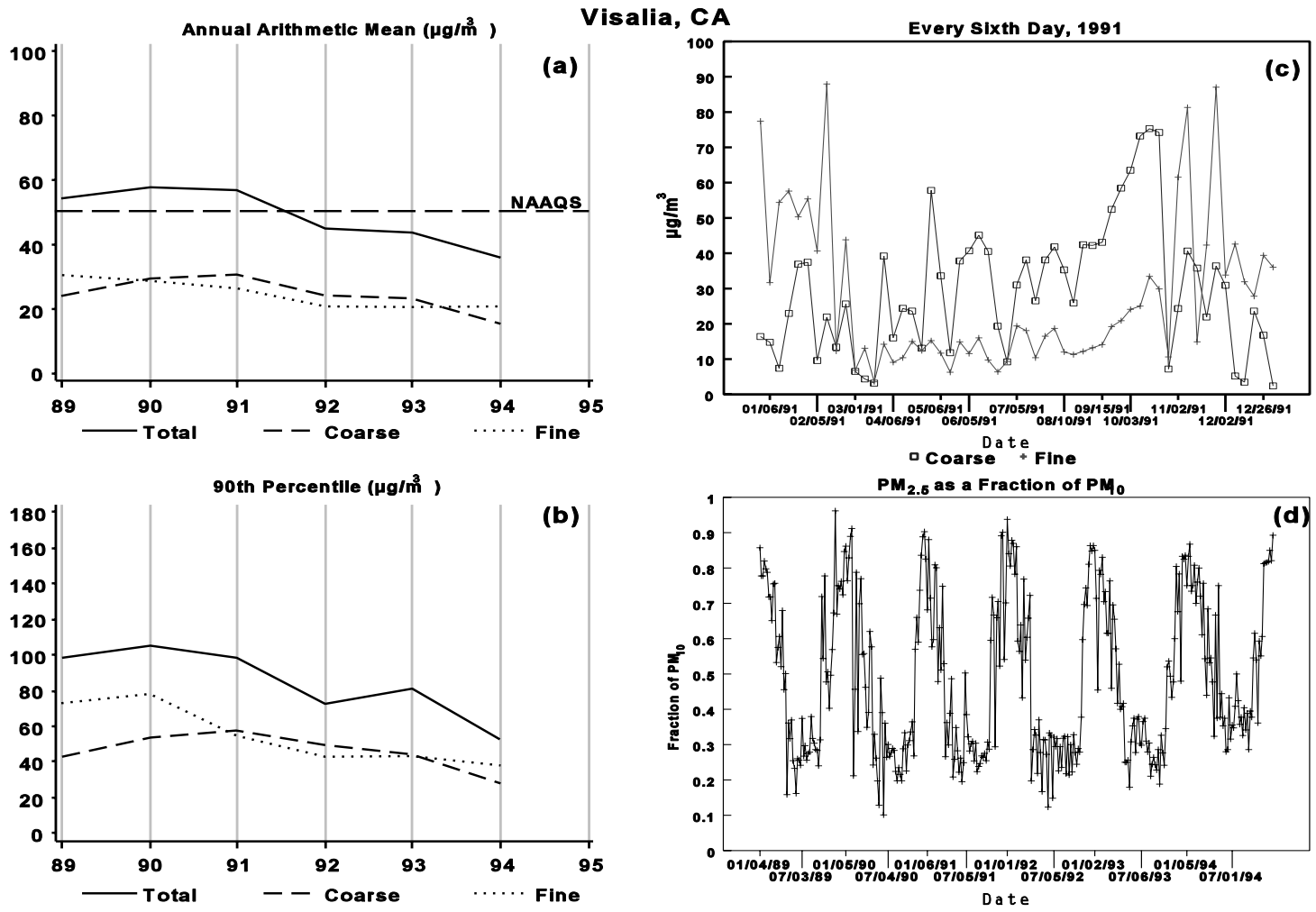

Figure 6-125. Trend data from Visalia from CARB: (a) Fine, coarse and total means; (b) Fine, coarse and total 90th percentiles; (c) Every sixth day fine and coarse mass for 1991; (d) Fine and coarse mass as a fraction of PM_{10}.

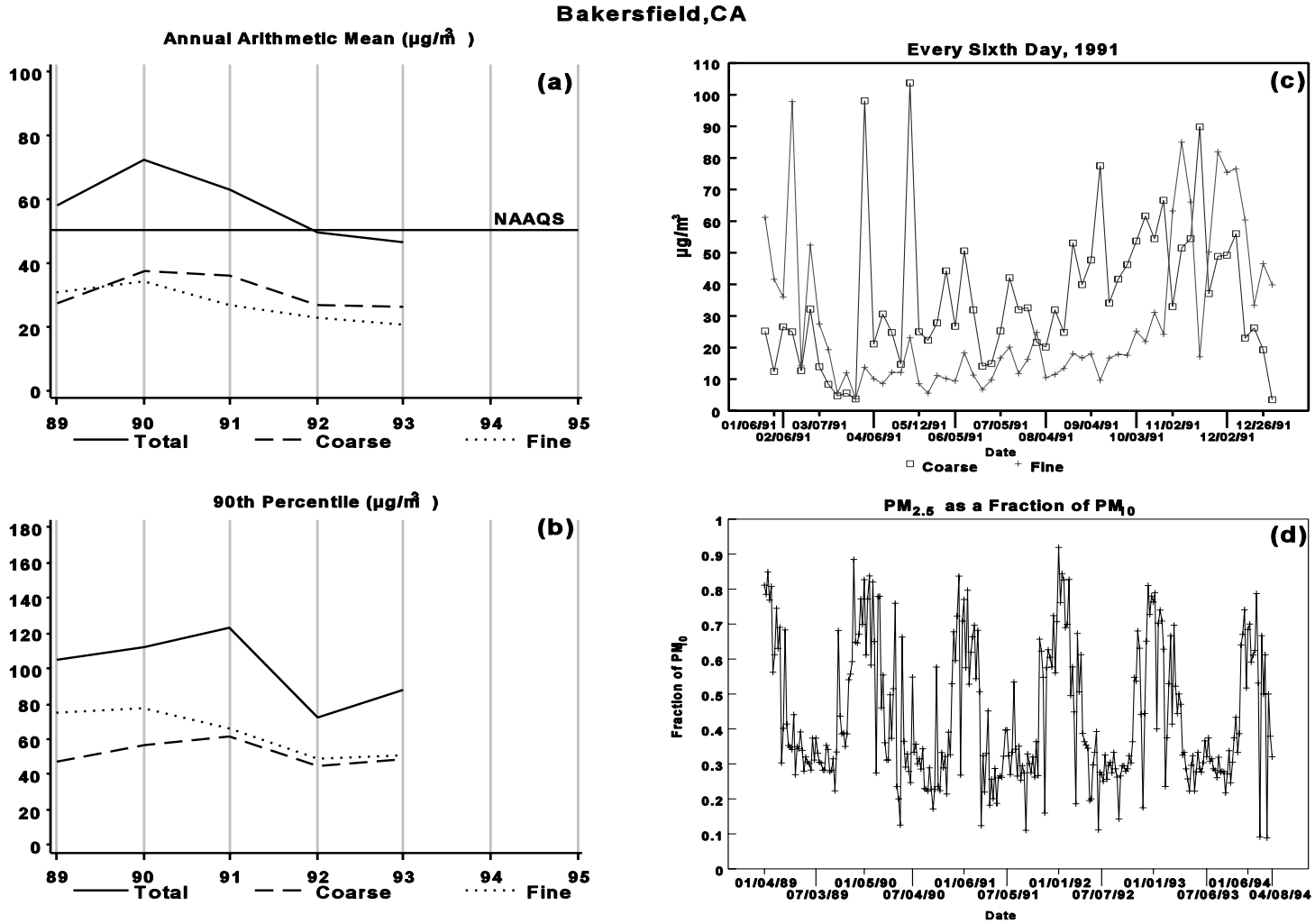

Figure 6-126. Trend data from Bakersfield from CARB: (a) Fine, coarse and total means; (b) Fine, coarse and total 90th percentiles; (c) Every sixth day fine and coarse mass for 1991; (d) Fine and coarse mass as a fraction of PM_{10}.

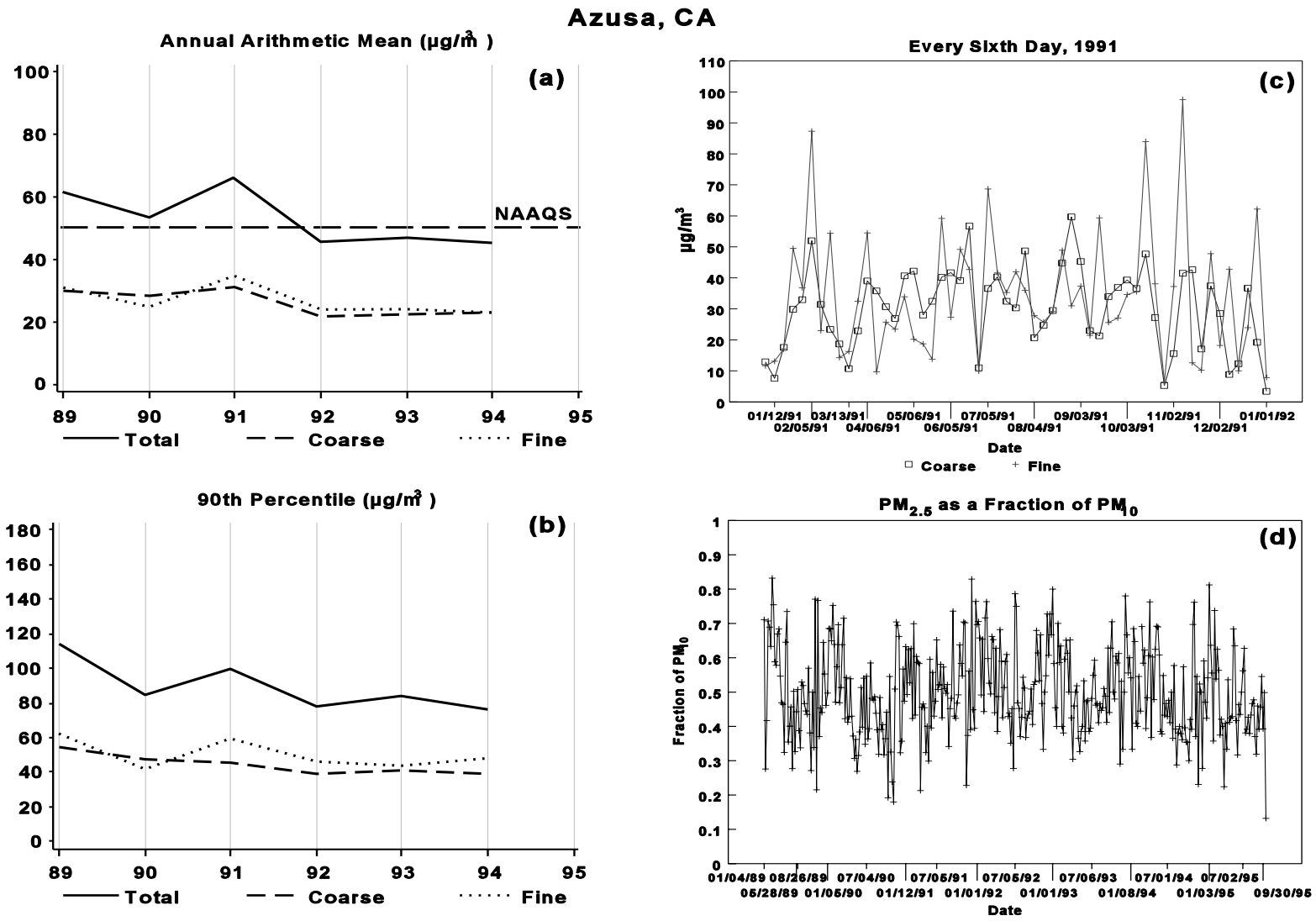

Figure 6-127. Trend data from Azusa from CARB: (a) Fine, coarse and total means; (b) Fine, coarse and total 90th percentiles; (c) Every sixth day fine and coarse mass for 1991; (d) Fine and coarse mass as a fraction of PM_{10}.

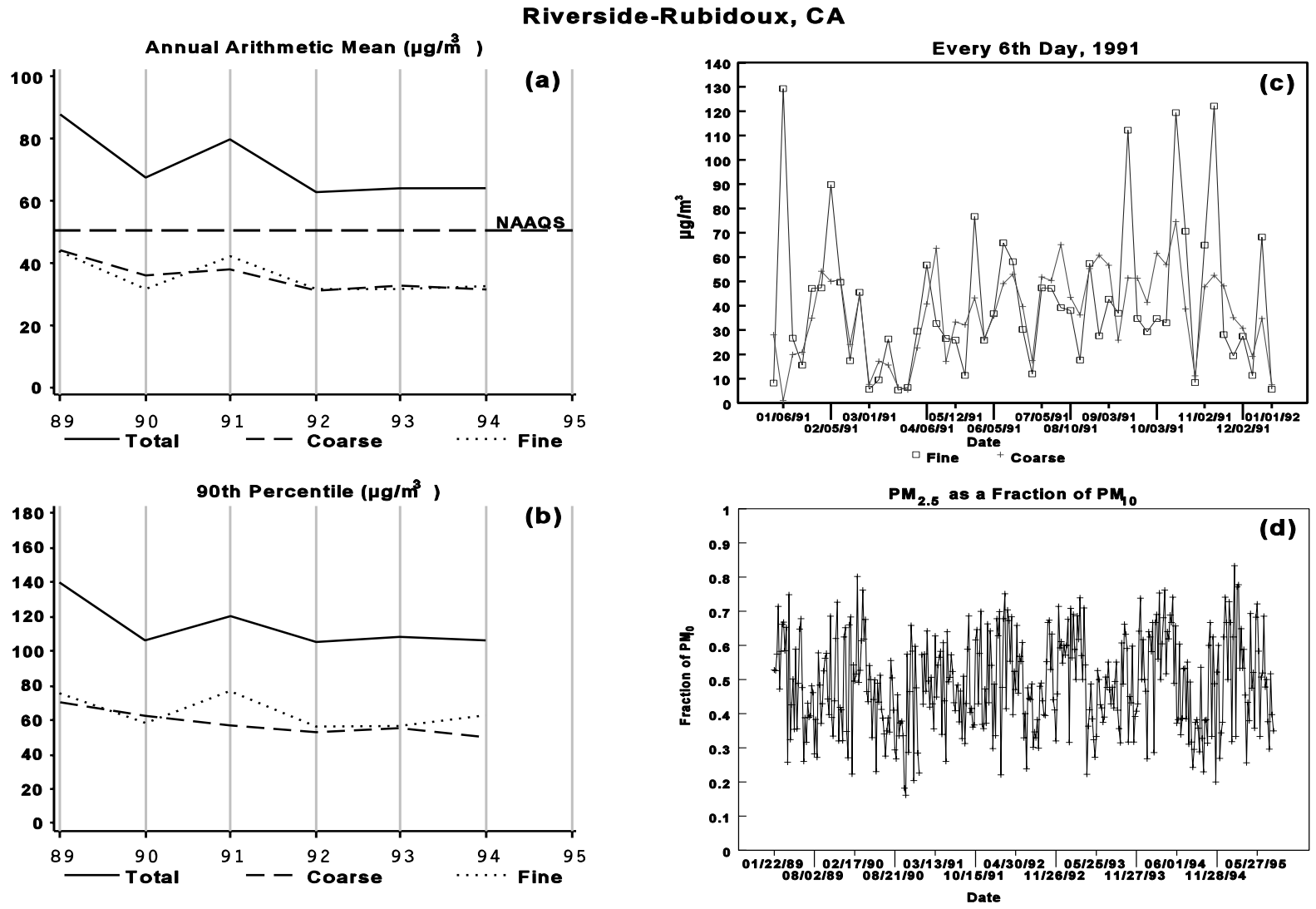

Figure 6-128. Trend data from Riverside-Rubidoux from CARB: (a) Fine, coarse and total means; (b) Fine, coarse and total 90th percentiles; (c) Every sixth day fine and coarse mass for 1991; (d) Fine and coarse mass as a fraction of PM_{10}.

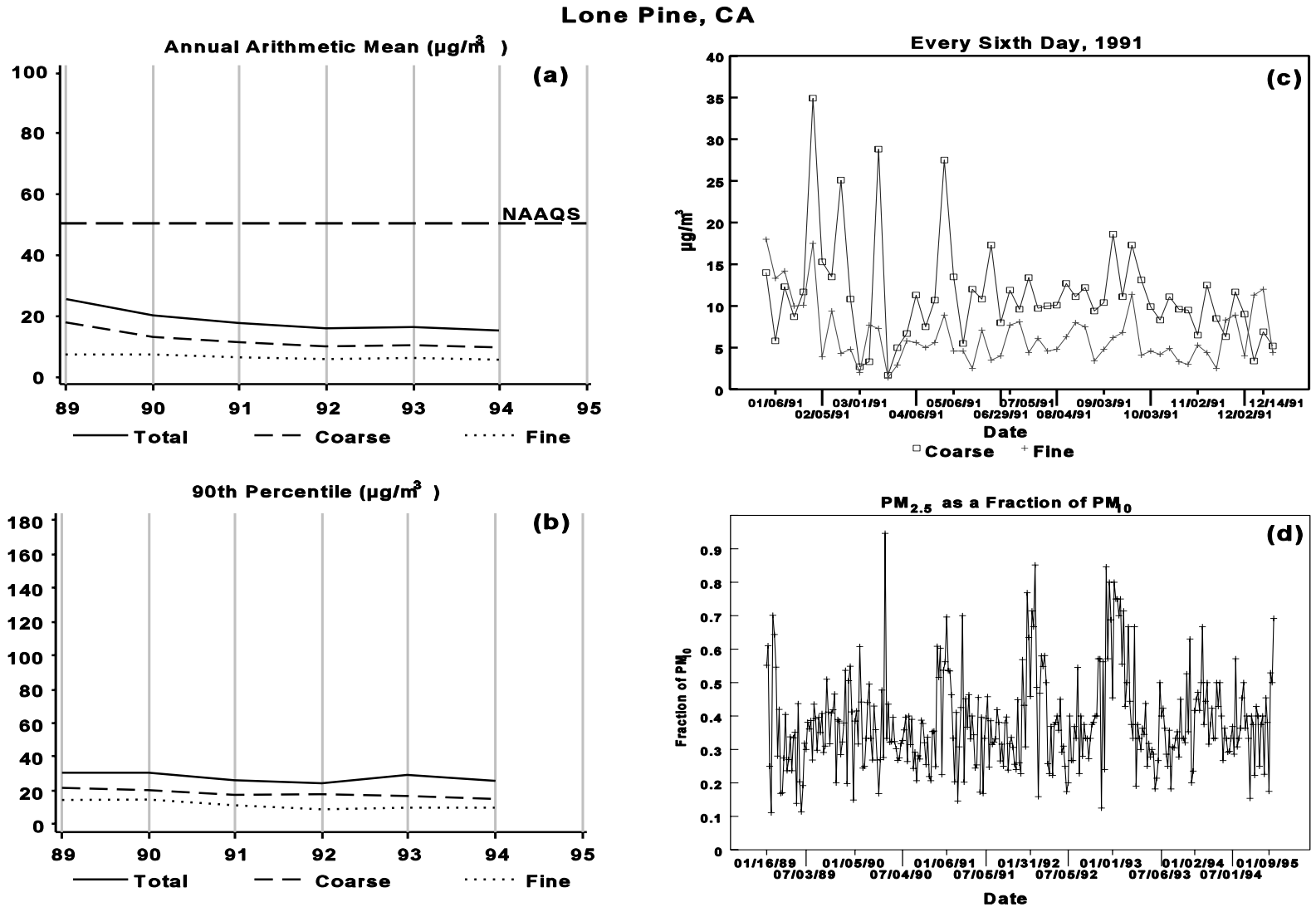

Figure 6-129. Trend data from Lone Pine from CARB: (a) Fine, coarse and total means; (b) Fine, coarse and total 90th percentiles; (c) Every sixth day fine and coarse mass for 1991; (d) Fine and coarse mass as a fraction of PM_{10}.

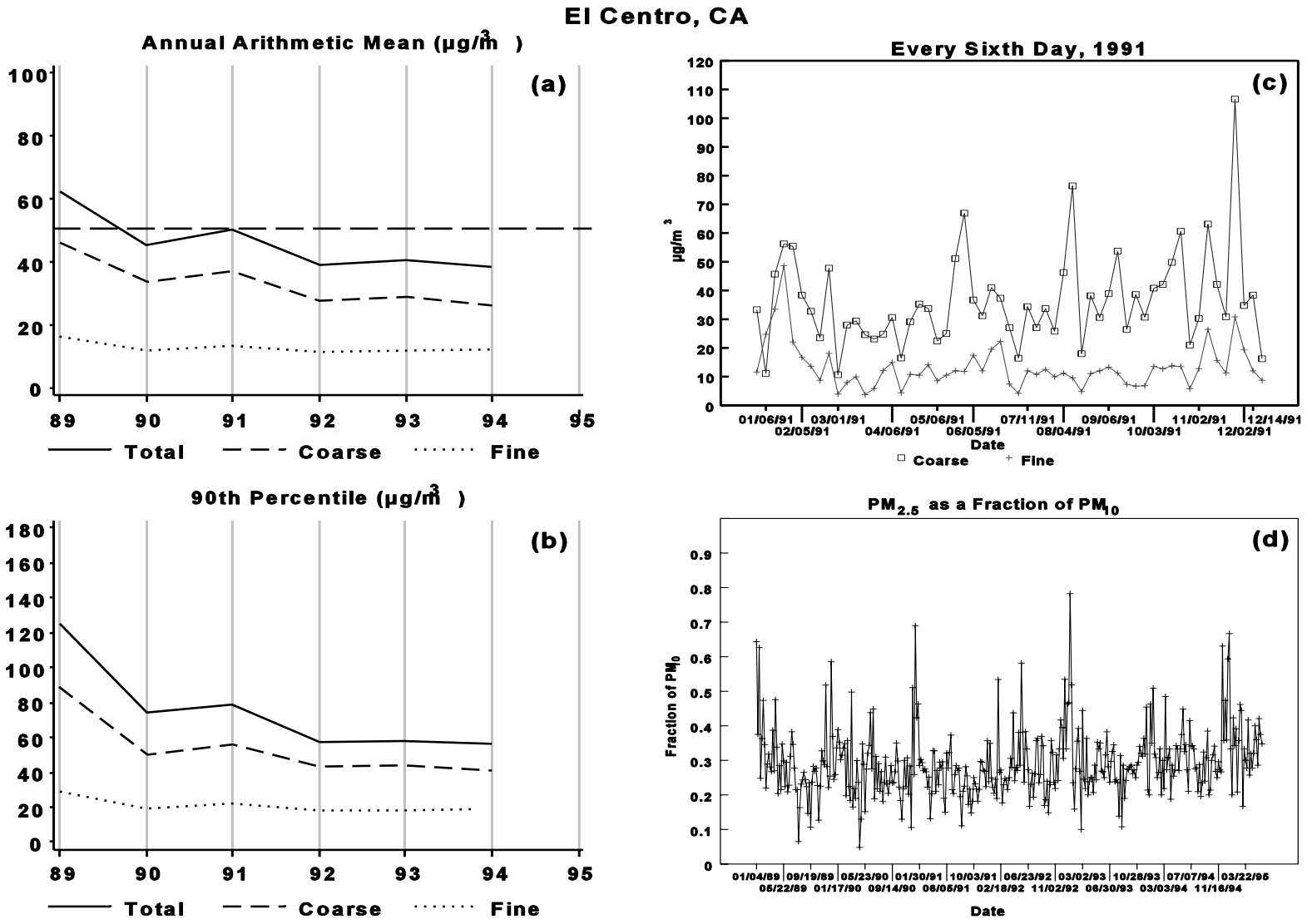

Figure 6-130. Trend data from El Centro from CARB: (a) Fine, coarse and total means; (b) Fine, coarse and total 90th percentiles; (c) Every sixth day fine and coarse mass for 1991; (d) Fine and coarse mass as a fraction of PM_{10}.

TABLE 6-11. MAXIMUM VALUE; 2ND, 3RD, 4TH, AND 5TH HIGHEST VALUES; 98TH AND 95TH PERCENTILE VALUES; 50TH PERCENTILE VALUE (MEDIAN); Δ, THE DIFFERENCE BETWEEN THE MEDIAN AND THE MAXIMUM VALUES AND #, THE NUMBER OF MEASUREMENTS AVAILABLE FROM EIGHT CALIFORNIA AIR RESOURCES BOARD SITES: (a) $PM_{2.5,}$ (b) $PM_{(10-2.5)}$, and (c) PM_{10}

					$PM_{2.5}$					
SITE	Max	2nd	3rd	4th	5th	98%	95%	50%	Δ	#
Riverside	142	130	129	122	121	114	77	29	113	368
Azusa	98	95	88	88	87	84	60	23	75	371
Bakersfield	447	147	119	100	98	93	77	16	431	296
Visalia	140	121	105	91	91	82	69	15	125	389
Stockton	94	92	91	75	75	70	55	11	83	381
San Jose	105	88	86	69	66	59	44	9	96	341
El Centro	73	62	52	49	47	39	26	11	62	392
Lone Pine	29	23	22	19	18	17	13	6	23	322
					$PM_{(10-2.5)}$					
Riverside	123	114	87	86	86	76	68	34	89	368
Azusa	108	98	71	62	61	57	50	24	84	371
Bakersfield	320	104	99	98	90	76	61	27	293	296
Visalia	86	75	74	73	70	64	51	21	65	389
Stockton	66	57	57	56	56	54	41	16	50	381
San Jose	55	45	41	39	32	64	51	11	44	341
El Centro	324	176	160	150	132	108	63	27	297	392
Lone Pine	107	105	84	71	67	42	26	10	97	322
					PM_{10}					
Riverside	194	189	189	182	182	178	130	68	126	368
Azusa	203	152	139	139	135	127	99	50	153	371
Bakersfield	766	218	183	163	144	135	120	48	718	296
Visalia	187	164	138	137	130	109	98	43	144	389
Stockton	126	119	112	110	102	98	82	30	96	381
San Jose	151	109	102	87	85	76	61	22	129	341
El Centro	347	228	222	167	158	130	90	39	308	392
Lone Pine	122	120	101	93	76	54	36	16	106	322

TABLE 6-12. MAXIMUM VALUE; 2ND, 3RD, 4TH, AND 5TH HIGHEST VALUES; 98TH AND 95TH PERCENTILE VALUES; 50TH PERCENTILE VALUE (MEDIAN); Δ, THE DIFFERENCE BETWEEN THE MEDIAN AND THE MAXIMUM VALUES AND #, THE NUMBER OF MEASUREMENTS AVAILABLE FOR STIES IN PHILADELPHIA FROM 1979 TO 1995: (a) $PM_{2.5,}$ (b) $PM_{(10-2.5)}$, and (c) PM_{10},AND (d) TSP

Philadelphia											
						$PM_{2.5}$					
Site	Dates	Max	2nd	3rd	4th	5th	98%	95%	50%	Δ	#
IPN Average	3/79 12/83	98	94	74	65	65	61	50	21	74	366
IPN S. Broad	3/82 12/83	54	54	52	50	50	53	50	22	32	91
AIRS	1/87 12/90	55	55	47	46	45	46	43	18	37	219
Harvard PBY	5/92 5/59	73	72	56	53	53	43	36	15	58	1014
						$PM_{(10-2.5)}$					
IPN Average	3/79 12/83	NA	NA	NA	NA	NA	NA	NA	NA	NA	0
IPN S. Broad	3/82 12/83	28	25	20	19	17	25	18	9	19	91
AIRS	1/87 12/90	39	39	38	37	30	37	25	12	27	219
Harvard PBY	5/92 5/59	40	28	27	25	24	18	15	6	34	970
						PM_{10}					
IPN Average	3/79 12/83	NA	NA	NA	NA	NA	NA	NA	NA	NA	0
IPN S. Broad	3/82 12/83	71	66	66	65	64	67	64	30	41	91
AIRS	1/87 12/90	86	83	82	79	73	79	60	31	55	219
Harvard PBY	5/92 5/59	82	78	72	64	64	54	48	22	60	1025
						TSP					
IPN Average	3/79 12/83	196	150	148	140	138	129	114	64	132	366
IPN S. Broad	3/82 12/83	116	107	105	101	99	109	100	61	55	91
AIRS	1/87 12/90	131	124	116	116	112	116	104	56	75	219
Harvard PBY	5/92 5/59	NA	NA	NA	NA	NA	NA	NA	NA	NA	0

and 5th highest values; the 98th and 95th percentile values; the 50th percentile (median value) and the difference between the median and the maximum value are given for the measurement period available at each site. The maximum $PM_{2.5}$, $PM_{(10-2.5)}$, and PM_{10} levels were substantially higher at all the California sites, including the site at Lone Pine (estimated 1980 population, 1800), than at the Philadelphia sites. Differences between maximum and median levels are also larger at the California sites. The causes for the extremely high values observed at the Bakersfield site are not known. Data on the upper ranges of TSP are shown for Philadelphia sites as available.

6.10.3.2 Relationships Between $PM_{2.5}$; $PM_{(10-2.5)}$, PM_{10}, and TSP in Philadelphia

Epidemiologists have made extensive use of a long-term TSP data set from Philadelphia (Chapter 12; Wyzga and Lipfert, 1996; Li and Roth, 1995) to investigate the statistical relationships between TSP and mortality. It is possible, however, that $PM_{2.5}$ or PM_{10}, instead of TSP, may be the causal agent and that TSP may serve as an indicator for $PM_{2.5}$ or PM_{10}. PM indicators for Philadelphia, other than TSP, have not been available until recently. Therefore, an examination of relationships between TSP, $PM_{2.5}$, and PM_{10} in the Philadelphia area may provide data that will be useful in interpreting the epidemiological results obtained in Philadelphia with TSP. Such relationships are displayed in a series of Figures (6-131 to 6-135) that show: (Panel a) TSP plotted versus PM_x (where PM_x is either $PM_{2.5}$ or PM_{10}) (Panel b) the distribution of values of PM_x/TSP, (Panel c) PM_x/TSP plotted versus PM_x, and (Panel d) PM_x/TSP plotted versus TSP.

It would appear from Figures 6-131 to 6-135 that there is some relationship between PM_x and TSP and that the relationship improves at higher values of TSP. The PM_x/TSP ratio does not appear to vary significantly with PM_x. However, the ratio does appear to increase with TSP until a certain level of TSP is reached and then levels off. These visual observations are quantified by comparison of the PM_x/TSP ratios at various levels and statistical regressions of PM_x with various TSP fractions shown in Table 6-13.

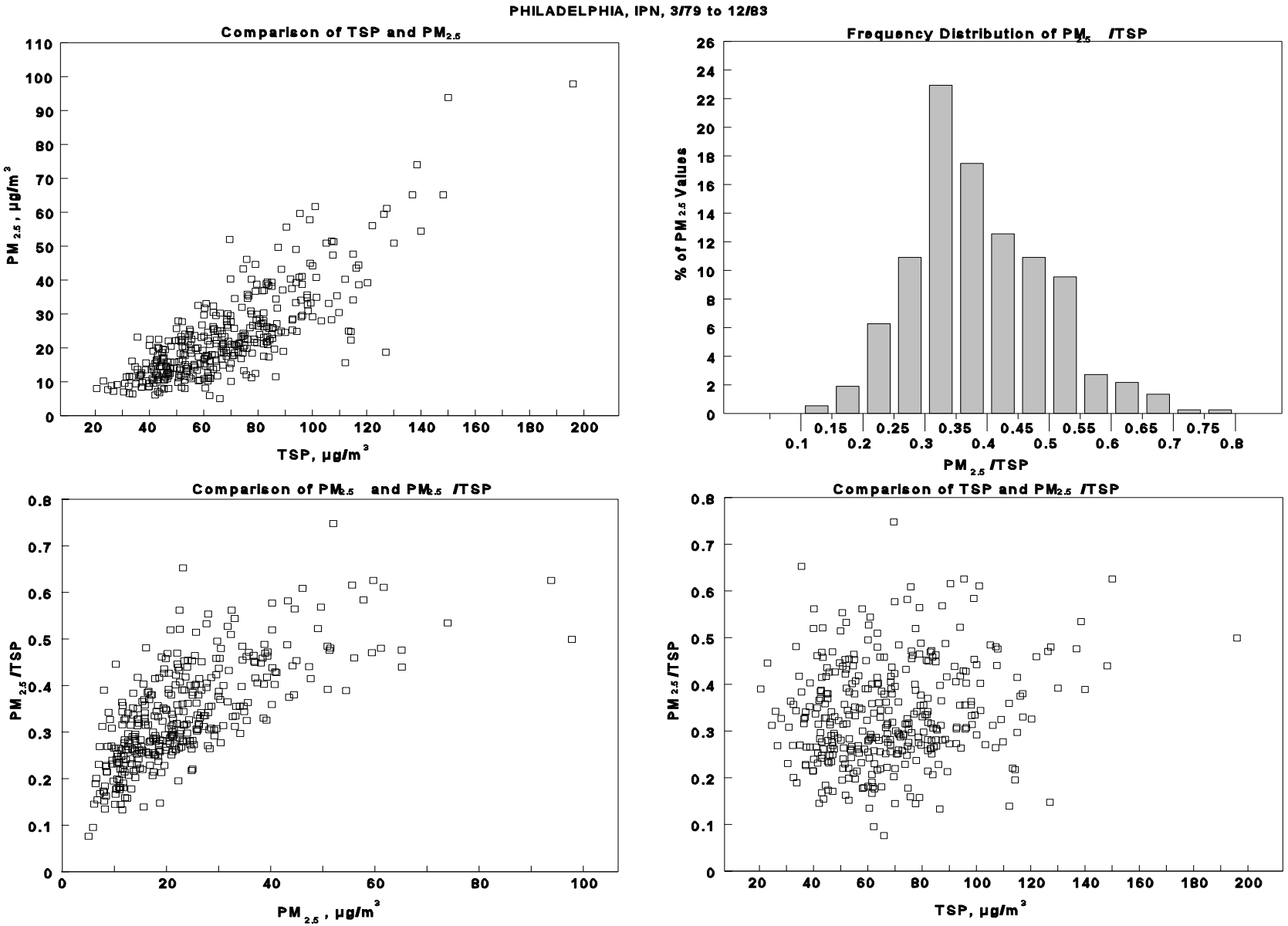

Figure 6-131. $PM_{2.5}$ and TSP Relationships in Philadelphia, IPN Average, 3/79 to 12/83: (a) comparison of $PM_{2.5}$ with TSP, (b) frequency distribution of $PM_{2.5}$/TSP, (c) comparison of $PM_{2.5}$ /TSP with $PM_{2.5}$, (d) comparison of $PM_{2.5}$/TSP with TSP.

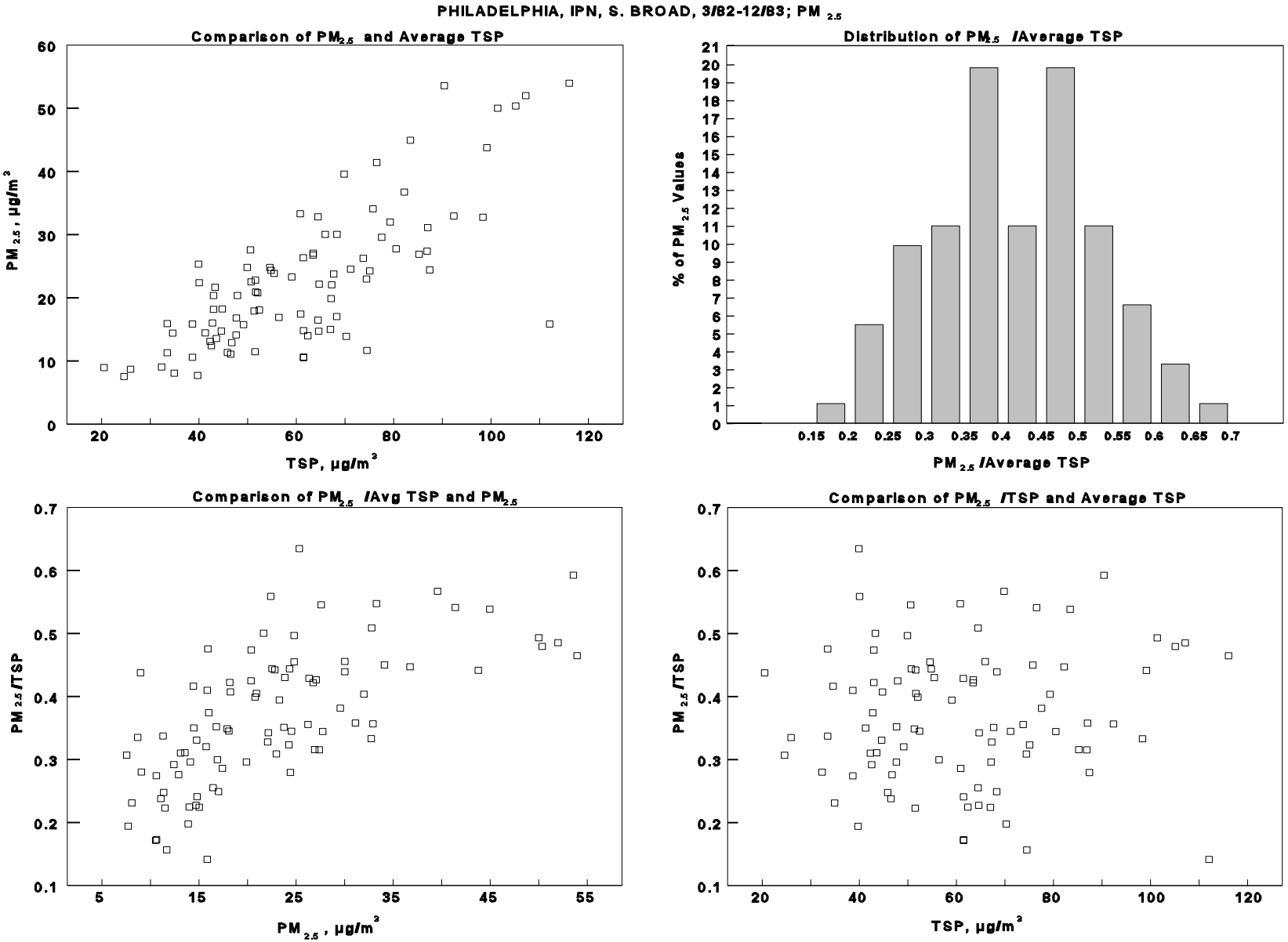

Figure 6-132. $PM_{2.5}$ and TSP Relationships in Philadelphia, IPN, South Broad Site, 3/82 to 12/83: (a) comparison of $PM_{2.5}$ with TSP, (b) frequency distribution of $PM_{2.5}$/TSP, (c) comparison of $PM_{2.5}$/TSP with $PM_{2.5}$, (d) comparison of $PM_{2.5}$/TSP with TSP.

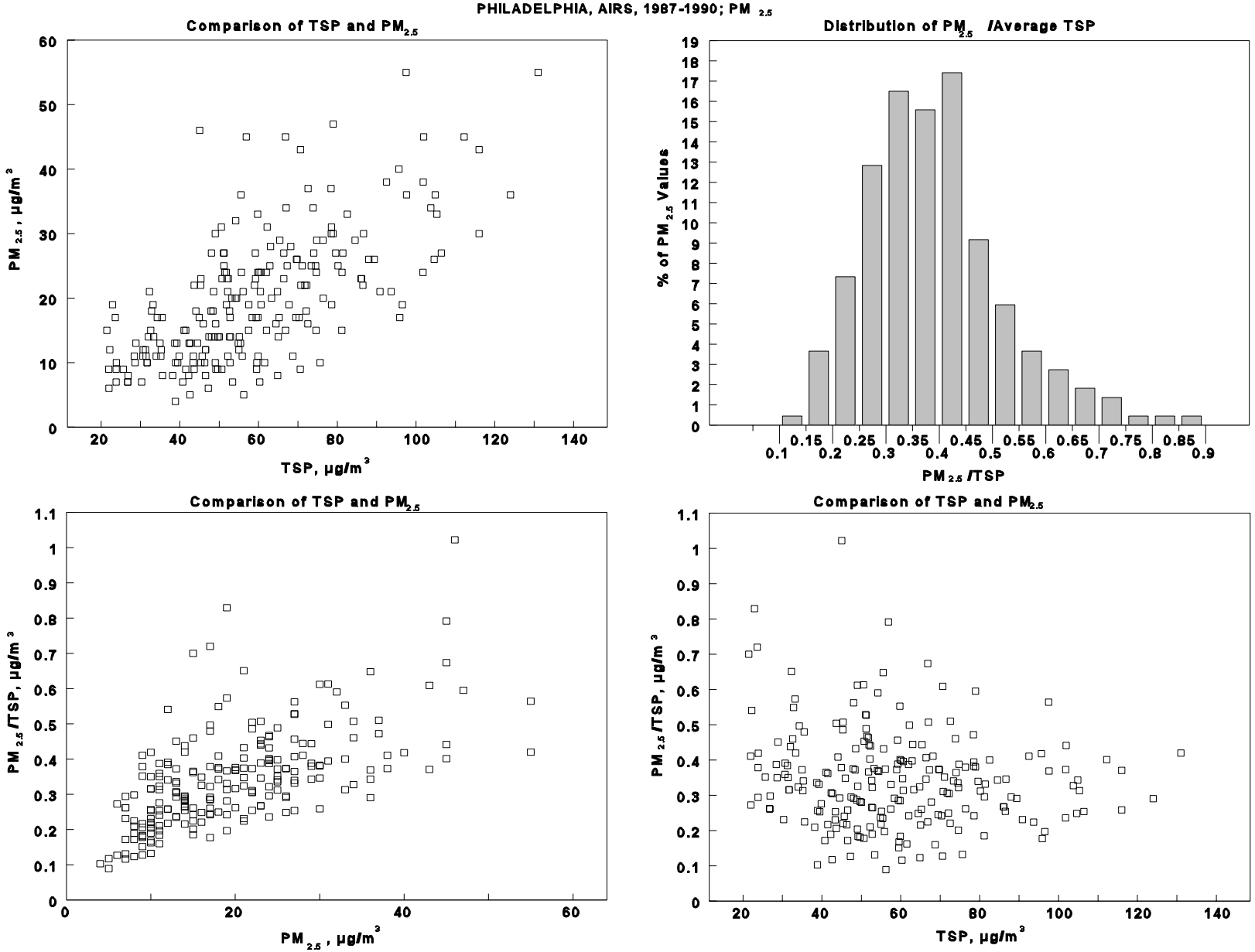

Figure 6-133. $PM_{2.5}$ and TSP Relationships in Philadelphia, AIRS, 1987 to 1990: (a) comparison of $PM_{2.5}$ with TSP, (b) frequency distribution of $PM_{2.5}$/TSP, (c) comparison of $PM_{2.5}$ /TSP with $PM_{2.5}$, (d) comparison of $PM_{2.5}$//TSP with TSP.

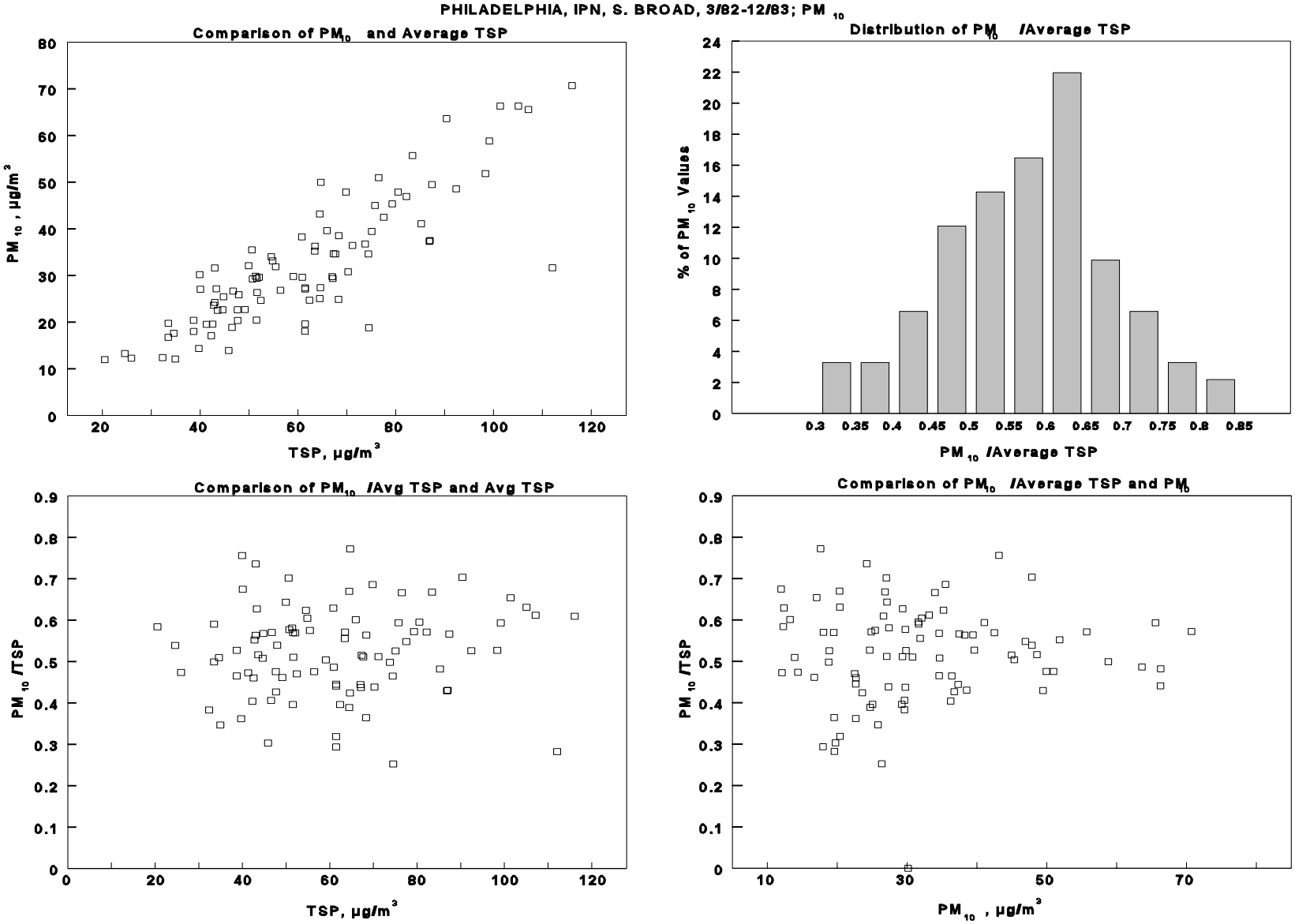

Figure 6-134. PM_{10} and TSP Relationships in Philadelphia, IPN, South Broad Site, 3/82 to 12/83: (a) comparison of PM_{10} with TSP, (b) frequency distribution of PM_{10}/TSP, (c) comparison of PM_{10}/TSP with PM_{10}, (d) comparison of PM_{10}/TSP with TSP.

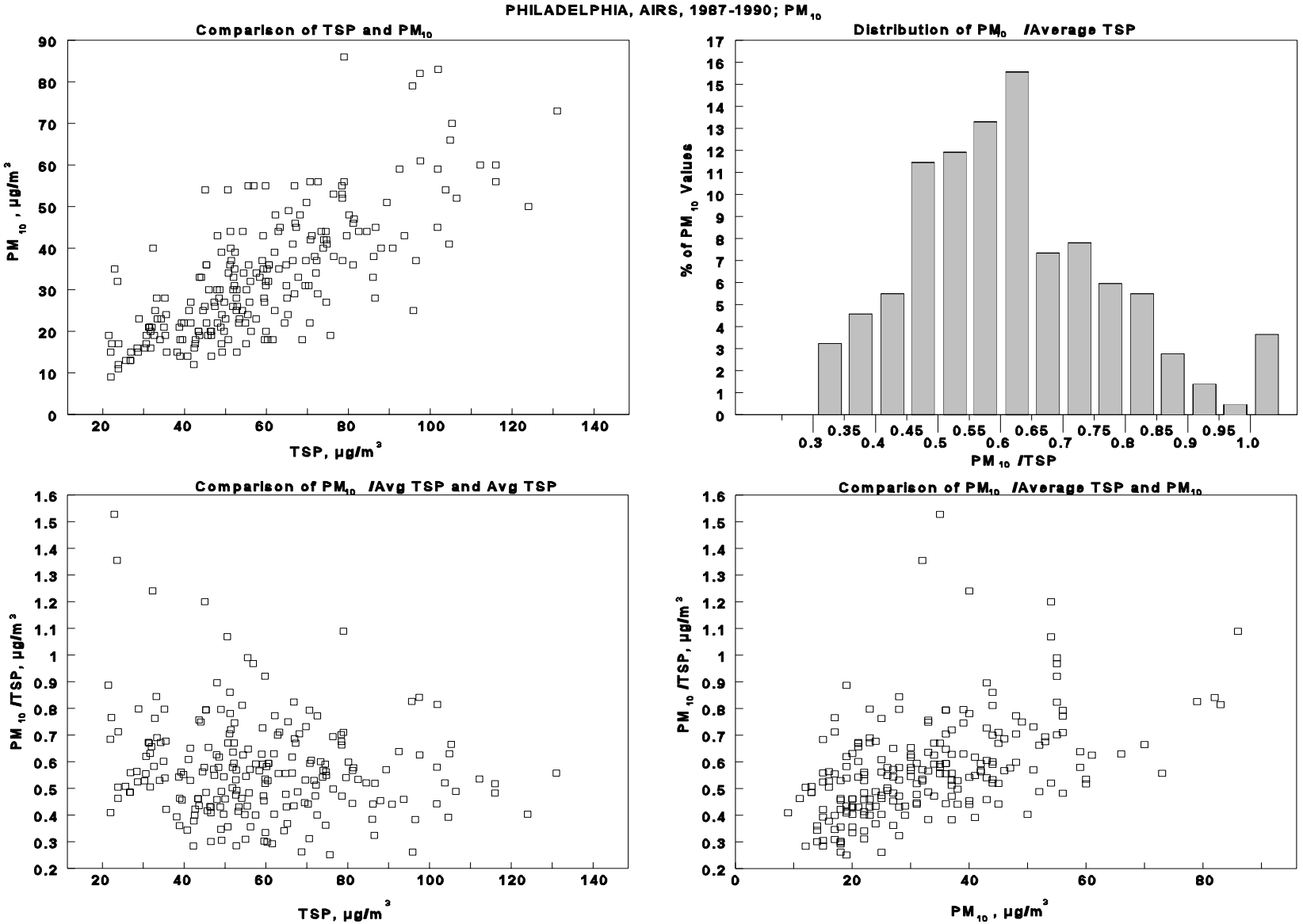

Figure 6-135. PM_{10} and TSP Relationships in Philadelphia, AIRS, 1987 to 1990: (a) comparison of PM_{10} with TSP, (b) frequency distribution of PM_{10}/TSP, (c) comparison of PM_{10}/TSP with PM_{10}, (d) comparison of PM_{10}/TSP with TSP.

TABLE 6-13. RELATIONSHIPS BETWEEN PM_X ($PM_{2.5}$ OR PM_{10}) AND TSP AS A FUNCTION OF TSP CONCENTRATION LEVELS FOR SEVERAL SITES IN PHILADELPHIA: (a) RATIO OF PM_x TO TSP, (b) COEFFICIENT OF DETERMINATION (R_2)

(a) Ratio of PM_x/TSP

		$PM_{2.5}$/TSP			PM_{10}/TSP		
Philadelphia		TSP	TSP	TSP	TSP	TSP	TSP
Site	Dates	All	<80	>80	All	<80	>80
IPN Average	3/79 12/83	0.335 ± 0.108	0.325 ± 0.107	0.363 ± 0.107	NA	NA	NA
IPN S. Board	3/82 12/83	0.371 ± 0.105	0.361 ± 0.106	0.416 ± 0.090	0.525 ± 0.105	0.516 ± 0.107	0.573 ± 0.079
AIRS	1/87 12/90	0.345 ± 0.137	0.350 ± 0.114	0.317 ± 0.083	0.573 ± 0.187	0.581 ± 0.194	0.528 ± 0.131

(b) Coefficients of Determination, R^2

		$PM_{2.5}$ with			PM_{10} with		
Philadelphia		TSP	TSP	TSP	TSP	TSP	TSP
Site	Dates	All	<80	>80	All	<80	>80
IPN Average	3/79 12/83	0.64	0.36	0.50	NA	NA	NA
IPN S. Board	3/82 12/83	0.57	0.38	0.48	0.78	0.57	0.61
AIRS	1/87 12/90	0.45	0.29	0.34	0.55	0.42	0.24

6.10.3.3 Correlations Between $PM_{2.5}$, $PM_{(10-2.5)}$, and PM_{10}

The analysis of epidemiological results suggest that the smaller size fraction of particulate matter may have a stronger association with health outcomes than fractions that contain larger size particles (Chapter 12). It is of interest, therefore, to examine the correlations between $PM_{2.5}$, $PM_{(10-2.5)}$, and PM_{10}. The means of these fractions and the coefficient of determinination, R^2, for their relationships are shown in Table 6-14 for eight sites in California (CARB, 1995) and in Table 6-15 for several sites and times for Philadelphia (IPN, 1985; AIRS, 1995; Harvard, 1995).

If correlation between $PM_{2.5}$ and PM_{10} is high but the correlation of $PM_{(10-2.5)}$ with both $PM_{2.5}$ and PM_{10} is low, it is possible that PM_{10} is serving as an indicator of $PM_{2.5}$ and that any health effects of $PM_{(10-2.5)}$ would be masked by the larger $PM_{2.5}$ (Wilson and Suh, 1996). This may be the case in Philadelphia since $PM_{2.5}$ to PM_{10}. In general, $PM_{(10-2.5)}$ is a larger fraction of PM_{10} at the California sites than at the Philadelphia site. However, there is still substantial variability (~40% from minimum to maximum) in this ratio in the data sets from California. Correlations between $PM_{2.5}$ and $PM_{(10-2.5)}$ are highly variable at the sites in California and encompass the Philadelphia value. The large correlations seen between $PM_{2.5}$ and $PM_{(10-2.5)}$ at several California sites suggest a significant contribution from crustal material to $PM_{2.5}$. In contrast, at the Philadelphia site, only $PM_{2.5}$ and not $PM_{(10-2.5)}$ was highly correlated with PM_{10}. These data support the desirability of having independent data on fine mode particles and coarse mode particles for epidemiological investigations.

6.10.3.4 Fine Fraction

The fine fractions of PM_{10} ($PM_{2.5}/PM_{10}$) were shown for Philadelphia in Figure 6-116 (Panels c and d) and for California sites in Figures 6-123 to 6-130. A strong seasonal variation is evident at the California sites but not in Philadelphia. Numerical values of the $PM_{2.5}$ fractional contribution to PM_{10} are given for Philadelphia and for several California sites in Table 6-16. These variations in $PM2.5/PM_{10}$ demonstrate the difficulty of inferring $PM_{2.5}$ from PM_{10} measurements unless some information is available on $PM_{2.5}/PM_{10}$ on a seasonal and geographic basis.

TABLE 6-14. MEANS AND STANDARD DEVIATIONS FOR $PM_{2.5}$, $PM_{(10-2.5)}$, AND PM_{10} AND COEFFICIENTS OF DETERMINATION (R^2) BETWEEN PAIRS FOR EIGHT CALIFORNIA AIR RESOURCES BOARD SITES DURING THE PERIOD 1989 TO 1990

	Mean ± Standard Deviation		
Site	$PM_{2.5}$	$PM_{(10-2.5)}$	PM_{10}
Riverside	34.1 ± 24.3	34.5 ± 19.5	68.6 ± 37.6
Azusa	25.9 ± 17.2	25.5 ± 14.5	51.3 ± 27.7
Bakersfield	24.2 ± 24.2	33.7 ± 33.6	57.0 ± 27.7
Visalia	23.0 ± 20.5	23.3 ± 15.9	46.3 ± 26.7
Stockton	17.4 ± 16.7	17.8 ± 10.8	35.6 ± 21.8
San Jose	13.9 ± 14.1	11.9 ± 6.7	25.8 ± 17.9
El Centro	12.3 ± 8.2	31.5 ± 25.4	43.8 ± 30.5
Lone Pine	6.5 ± 3.7	12.1 ± 11.7	18.6 ± 13.8
	Coefficient of Determination, R^2		
Site	$PM_{2.5}$ to $PM_{(10-2.5)}$	$PM_{2.5}$ to PM_{10}	$PM_{(10-2.5)}$ to PM_{10}
Riverside	0.21	0.79	0.67
Azusa	0.27	0.79	0.71
Bakersfield	0.36	0.86	0.74
Visalia	0.36	0.66	0.41
Stockton	0.05	0.77	0.44
San Jose	0.16	0.88	0.48
El Centro	0.27	0.50	0.94
Lone Pine	0.19	0.42	0.94

TABLE 6-15. MEANS AND STANDARD DEVIATIONS FOR $PM_{2.5}$, $PM_{(10-2.5)}$, PM_{10}, and TSP AND COEFFICIENTS OF DETERMINATION (R^2) BETWEEN PAIRS FOR SEVERAL SITES IN PHILADELPHIA DURING PERIODS FROM 1979 TO 1995

Philadephia		Mean ± Standard Deviation			
Site	Dates	$PM_{2.5}$	$PM_{(10-2.5)}$	PM_{10}	TSP
IPN Average	3/79 12/83	23.3 ± 13.3	NA	NA	68.2 ± 24.7
IPN S. Board	3/82 12/83	22.6 ± 11.0	9.7 ± 4.7	32.1 ± 13.5	61.1 ± 20.5
AIRS	1/87 12/90	19.9 ± 10.0	13.1 ± 6.7	33.0 ± 14.9	58.4 ± 21.9
Harvard PBY	5/92 5/95	17.4 ± 9.4	7.0 ± 4.3	24.3 ± 11.5	NA

		Coefficient of Determination, R^2			
Site	Dates	$PM_{2.5}$ with $PM_{(10-2.5)}$	$PM_{2.5}$ with PM_{10}	$PM_{(10-2.5)}$ with PM_{10}	$PM_{2.5}$ with TSP
IPN Average	3/79 12/83	NA	NA	NA	0.64
IPN S. Board	3/82 12/83	0.14	0.90	0.42	0.57
AIRS	1/87 12/90	0.32	0.86	0.69	0.45
Harvard PBY	5/92 5/95	0.11	0.88	0.41	NA

6.11 SUMMARY AND CONCLUSIONS

This chapter presents ambient concentration measurements of particulate mass, PM_{10}, $PM_{2.5}$, and $PM_{(10-2.5)}$, and of the chemical composition of particulate matter. For PM_{10} measurements the number of urban monitoring stations in the AIRS network increased rapidly in the years immediately after 1985, but the increase slowed substantially in the early 1990s. The measurements of PM_{10} at most of these stations were made every 6th day. Measurements

TABLE 6-16. $PM_{2.5}/PM_{10}$ (FRACTION OF PM_{10} CONTRIBUTED BY $PM_{2.5}$)

	Mean	Standard Deviation	Coefficient of Variation (%)	Range
Philadelphia	0.71	0.13	18	
Mar-May	0.73	0.14	19	0.09-1.09
Jun-Aug	0.73	0.16	22	0.30-1.56
Sept-Nov	0.72	0.17	24	0.17-1.81
Dec-Feb	0.75	0.15	20	0.03-1.55
Azusa	0.50	0.13	26	
Visalia	0.49	0.22	45	
San Jose	0.49	0.15	31	
Riverside	0.49	0.14	29	
Stockton	0.46	0.18	39	
Bakersfield	0.44	0.19	43	
Lone Pine	0.38	0.14	37	
El Centro	0.29	0.10	34	
Riverside				
Winter	0.57	0.14	25	0.22-0.99
Spring	0.48	0.13	27	0.22-0.76
Summer	0.41	0.09	22	0.23-0.69
Fall	0.48	0.15	15	0.16-0.74

of chemical species in urban areas usually are obtained in special studies of limited duration. Data for chemical species in urban areas are discussed as appropriate in the text.

The mass concentration measurements in urban areas have been used to obtain (a) annual trends in PM_{10}, (b) ratios and correlations of $PM_{2.5}$ to $PM_{(10-2.5)}$ and PM_{10} and (c) seasonal variations in PM_{10}, $PM_{2.5}$, and $PM_{(10-2.5)}$.

The measurements at non-urban sites were collected at a much smaller number of locations relative to the number of urban stations by region. The geographical location of the sites in the IMPROVE/NESCAUM networks were not selected to optimize their locations relative to AIRS stations in the same region. As a result, not only are there small numbers of non-urban sites by region, but most of these sites are geographically well displaced from urban areas.

The non-urban concentration measurements include both mass and chemical composition so they were used to obtain (a) the variations in PM_{10}, $PM_{2.5}$, and $PM_{(10-2.5)}$ with month of the year, (b) the chemical balances for sulfates, organic carbon, elemental carbon, and soil with month of the year and (c) the variations in the concentrations of S, Se, and V and the S to Se ratio with month of the year.

From the urban and non-urban PM_{10} concentration measurements, an "urban excess" was obtained from the monthly differences in AIRS and IMPROVE/NESCAUM PM_{10} values. Because of the limitations mentioned above and the lack of tests of statistical significance, these "urban excess" values should be viewed as preliminary and used very cautiously with respect to quantitative results.

Additional sections of Chapter 6 include the following discussions: (1) the mass apportionment of chemical species obtained from a group of selected research studies of the chemical composition at locations in the eastern, central and western U.S.; (2) acid sulfate study results by (a) their geographical distribution in the U.S. and southern Canada, (b) spatial variations on a city and urban scale, (c) seasonal variations, (d) diurnal variations, and (e) indoor and personal monitoring relative to outdoor hydrogen ion concentration measurements; (3) particle number concentrations with emphasis on ultrafine particles; (4) some information on metals potentially present in ultrafine particles; and (5) information on fine and coarse PM trends and patterns for sites where both fine and coarse PM measurements were available.

Based on these various concentration measurements a considerable number of conclusions may be obtained. Many of these conclusions are limited by (a) the number of monitoring sites available, (b) their geographical location, (c) the frequency of measurement and (d) differences in methodology used between networks or stations as well as between individual studies of chemical composition.

Trends in PM_{10} mass concentration, averaged over regions or by city, usually indicate a substantial decrease in PM_{10} concentrations by year from 1988 to 1994. There are exceptions to this significant downward trend in Philadelphia and at some locations within the Southern California Basin. The trend plots shown in Chapter 6 have not been tested for statistical significance. The trend plots can also be influenced by the approach taken in the selection of stations. Since the number of stations increased rapidly between 1985 and 1990, the trends that might be obtained using early data could be biased by the added stations being influenced by

location towards higher or lower PM_{10} concentration measurements. For this document, the set of stations in operation from 1988 to 1994 was used to obtain PM_{10} concentration trends during this period. It should also be noted that meteorological influences which are known to be important for deducing trends of O_3 concentrations also may affect PM_{10} concentrations on a year-to-year basis.

Keeping the limitations mentioned above in mind, urban trend analyses for PM_{10} are presented using all stations in operation in a given year and the smaller set of trend stations in operation over the entire 1988 to 1994 time period. The range for the averaged decrease in PM_{10} between 1988 and 1994 at urban stations was: for the contiguous U.S., all sites, 24%, trend sites, 20%; for the eastern U.S., all sites, 16%, trend sites, 18%; and for the western U.S., all sites, 31%, trend sites 28%. There were appreciable differences between regions in the range of averaged decreases in PM_{10} between 1988 and 1994 with the decrease for urban stations in the northeast ranging from 18% (all) to 19% (trend) while in the industrial midwest the decreases ranged from 12% (all) to 19% (trend). The ranges of averaged decreases for the three western regions were from 27% to 37% (all) and 23% to 33% (trend). These decreases in PM_{10} concentrations resulted in 1994 annual average regional AIRS concentrations in the range of 25 $\mu g/m^3$ to 32 $\mu g/m^3$.

For individual cities, both between and within cities, the decreases in PM_{10} for individual stations could show substantial variability. In the Los Angeles Basin, 3 of 6 stations showed statistically significant downward trends in PM_{10} while other stations showed no significant trends. In the western U.S. several large cities showed larger downward trends in PM_{10} than the regional averages. PM2.5 and PM(10-2.5) or PM10 data, suitable for determining trends of both fine and coarse components of PM10, are available from only a few sites in the eastern United States and a few sites in California. While a general decrease is evident in both fine and coarse components of PM10 at most sites where data is available, it is not possible to ascertain differential trends in the two components.

A few attempts to infer various types of background levels of $PM_{2.5}$ and PM_{10} have been made. The backgrounds most relevant to the Criteria Document include a "natural" background which excludes all anthropogenic sources anywhere in the world, and a background which excludes anthropogenic sources in North America, but not elsewhere. Annual average natural background levels of PM_{10} have been estimated to range from 4 to 8 $\mu g/m^3$ in the western United

States and 5 to 11 μg/m^3 in the eastern United States. Corresponding $PM_{2.5}$ levels have been estimated to range from 1 to 4 μg/m^3 in the western United States and 2 to 5 μg/m^3 in the eastern United States. Twenty-four hour average concentrations may be substantially higher than the annual or seasonal average background concentrations presented in Chapter 6. The 24-hour averages are usually considered for control strategies while the annual and seasonal averages are suitable for risk analyses.

Based either on the correlation of individual values or on the average $PM_{2.5}$ to PM_{10} values, the annual ratios of $PM_{2.5}$ to PM_{10} from urban stations fell within a relatively narrow range of 0.55 to 0.6, for both the entire eastern and western U.S. However, for two regions, the upper midwest and southwest, the correlations yielded ratios of less than 0.2 while the average $PM_{2.5}$ to PM_{10} values yielded ratios between 0.3 and 0.4.

Ratios of $PM_{2.5}$ to $PM_{(10-2.5)}$ from urban stations can vary with season as well as between regions. In the northeast, southeast, and industrial midwest regions, there is appreciable uniformity with $PM_{2.5}$ exceeding $PM_{(10-2.5)}$ during all seasons of the year. In contrast, in the southwest, the $PM_{2.5}$ is less than the PM coarse during all seasons of the year. In the northwest and in southern California, $PM_{2.5}$ exceeds PM_{10} in the fall and winter with the reverse occurring in the spring and summer.

Measurements of the day to day variability in $PM_{2.5}$ and PM_{10} are available from only one site located in Philadelphia, PA. The data show day to day variations of 8.6±7.5 μg/m^3 for PM_{10}, 6.8±6.5 μg/m^3 for $PM_{2.5}$, and 3.7±3.4 μg/m^3 for $PM_{10-2.5}$ from May 1992 to April 1995. Maximum day to day differences were 50 μg/m^3 for PM_{10}, 55 μg/m^3 for $PM_{2.5}$, and 35 μg/m^3 for $PM_{(10-2.5)}$. The ratio of $PM_{2.5}$ to PM_{10} was 0.72±0.16 over the measurement period and the correlation between $PM_{2.5}$ and PM_{10} was 0.86 (R^2) suggesting that variability in $PM_{2.5}$ was forcing the variability in PM_{10}. Data collected by dichotomous samplers at several sites in California showed that $PM_{(10-2.5)}$ accounted for roughly half of PM_{10} and that both $PM_{2.5}$ and $PM_{(10-2.5)}$ were highly correlated with PM_{10}. Differences among the Philadelphia data set and the California data sets illustrate the dangers in extrapolating relations among different size fractions from one region of the country to other regions.

Comparisons of seasonal profiles of PM_{10} show summer peaks for both urban and nonurban sites in the northeast, southeast, and industrial midwest. These summer peaks usually, but not exclusively, are associated with the summer peaks in $PM_{2.5}$. The $PM_{2.5}$ concentrations at

non-urban sites in the northeast, southeast, and industrial midwest exceed the $PM_{(10-2.5)}$ concentrations in all seasons of the year, as is the case for urban stations. The northwest urban PM_{10} and $PM_{2.5}$ concentrations show a spring and early summer minimum with the highest values in fall and winter, while the non-urban PM_{10} and $PM_{2.5}$ concentrations show a summer peak similar to the seasonal profiles in the eastern U.S. In southern California, the urban PM_{10} and $PM_{2.5}$ seasonal profiles show fall peaks, while the non-urban seasonal profiles have a relatively flat maximum from spring into early fall. Again it must be emphasized that with so few nonurban sites in most regions any conclusions drawn from the comparisons above are very tentative for most regions of the U.S.

The every-sixth-day urban PM_{10} averaged concentrations for most regions of the United States ranged during 1990 to 1994 from 10 to 15 $\mu g/m^3$ up to 40 to 60 $\mu g/m^3$. The southern California region had PM_{10} values averaging up to 70 to 75 $\mu g/m^3$. Day-to-day variations in PM_{10} concentrations in Knoxville, TN, ranged from 10 to 20 $\mu g/m^3$, while in Missoula, MT, PM_{10} concentrations ranged from <10 to 120 to 140 $\mu g/m^3$ with one value over 200 $\mu g/m^3$.

A quantity termed an urban excess has been discussed extensively in the text of Chapter 6. In view of the distinctions discussed above between the number and geographical distribution of urban and non-urban sites, the quantitative results probably should be interpreted with considerable caution. While it is reasonable that additional sources within cities should increase PM_{10} concentrations significantly above those at non-urban sites, the quantitative differences can be sensitive to the location of the non-urban sites with respect to individual cities. The most striking feature of the urban excess is its large increase in the fall and winter in the western United States compared to the eastern United States.

The chemical compositions at the nonurban IMPROVE/NESCAUM sites are discussed within the earlier sections of Chapter 6. Later in Chapter 6 an independent evaluation of chemical composition is given based on a mixture of intensive studies at both urban and nonurban sites. The results from both approaches appear reasonably consistent in showing geographical variations in chemical composition.

Both approaches indicate that sulfate, presumably present either as $(NH_4)HSO_4$ or as $(NH_4)_2SO_4$, is the largest contributor to the chemical species measured in the eastern United States. Other results indicate that a large regional background of sulfate is superimposed

on a smaller urban contribution. Results also indicate that sulfate is relatively uniform in concentration throughout much of the eastern United States. These results are less pronounced in the late fall and winter months. The contribution of sulfate to PM_{10} is somewhat smaller than sulfate is to $PM_{2.5}$. Comparisons of the eastern United States with the central United States and western United States show a decreasing contribution of sulfate to the chemical composition. Conversely, the soil and/or mineral concentrations become an increasingly important contributor to PM_{10} and $PM_{2.5}$ going from the eastern to the western United States. The nitrates, as NH_4NO_3, also appear to be a much more important contributor to the composition in areas of the western United States than in the eastern United States. Organic compounds also appear to increase in importance relative to sulfate going from the eastern to the western United States. For $PM_{(10-2.5)}$, sulfates are relatively unimportant. Soil or mineral components dominate the $PM_{(10-2.5)}$, but there is a substantial unknown fraction of $PM_{(10-2.5)}$.

Particle strong acidity, defined as H_2SO_4 plus HSO_4^-, is a regional pollutant fairly evenly distributed across large areas of the central portion of the eastern United States. It is relatively evenly distributed across small cities, but in the one large urban area from which results have been reported, the higher concentrations of ammonia in the central city apparently neutralize a significant portion of the acidity. Thus, higher concentrations of acidity are found in rural areas, small towns, and suburban areas than in the centers of larger urban areas. The concentration of acidity is higher in the summer and peaks during the early afternoon in urban areas. Indoor, outdoor, and personal monitoring indicates that indoor and personal concentrations of acidity are lower than outdoor concentrations, presumably due to neutralization by indoor ammonia. Particle strong acidity is normally found exclusively in the fine particle mode. Coarse particles tend to be basic. Exceptions may occur during periods of fog or very high relative humidity.

The number concentration of particles is generally dominated by particles below 0.1 μm or 100 nm in diameter, termed ultrafine particles. When a distinct mode is present, it is called the nuclei mode. Number geometric mean diameter ranged from 12 to 43 nm in Long Beach, CA and 47 to 75 nm in clean air in the Rocky Mountains. Particle number concentrations varied from less than 1,000/cm^3 at clean background sites to over 100,000/cm^3 in polluted urban areas and were correlated with the volume of particles below 0.1 μm. Particle number concentrations were not found to be correlated with accumulation mode volume on an hourly basis.

Correlations of particle number and accumulation mode volume might be expected if compared over longer time intervals (e.g., days), but such studies have not yet been done.

An examination of the size distribution of metals suggests that metals that may be volatilized during combustion may appear as ultrafine particles. Such metals include copper, zinc, and lead and possibly nickel and vanadium, as well as nonmetals selenium and sulfur. Ultrafine particles appear to exist longer under conditions of low concentrations and high relative humidity.